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CVIII.—ON THE CAUSE OF THE RETENTION AND RELEASE OF GASES OCCLUDED BY THE OXIDES OF METALS.[1]

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In a recent critical discussion of Stas' work upon the atomic weight of carbon, Dr. Alexander Scott,[2] of London, had occasion to repeat some observations made at Harvard several years ago.[3] According to these observations, cupric oxide made from cupric nitrate had been found usually to contain several times its volume of occluded gases, chiefly nitrogen, and moreover it was shown that this gas resulted from the decomposition of minute traces of residual nitrate confined in the inmost recesses of the masses of oxide. Dr. Scott, however, could not find as much as one-tenth of this amount of gas in his material. Since he was unable to explain the apparent discrepancy, it is one of the objects of the present paper to shed a clearer light upon the subject.

The essential point which escaped Dr. Scott's notice is this: the temperature of ignition is the most important condition determining the amount of the occluded gases. When the

[1] The greater part of this paper was presented to the American Academy of Arts and Sciences on March 9, 1898, and is published in its Proceedings.

[2] J. Chem. Soc. Trans., **71**, 559, (1897).

[3] Proc. Am. Acad., **26**, 281; Ztschr. anorg. Chem., **1**, 196.

temperature is very high, nearly all of the imprisoned impurity is set free. To quote Dr. Scott's words, his oxide was exposed "for varying times to a full red heat in a muffle heated with gas." It is well known that at a temperature of about 1000°, cupric oxide melts with a very considerable loss of oxygen. It is obvious, then, that temperatures in this neighborhood are quite out of the question when the atomic weight of copper is concerned; and this constant was the chief subject of the old investigation. Hence, among the many experiments made by me in 1891, only three dealt with material which had been heated above 700°. The evidence of these three experiments (Nos. 59, 81, and 95), is unanimous in showing that most of the occluded impurity is set free at bright redness, and the first two of them agree quantitatively with the results of Dr. Scott.

Although it is thus evident that the English and American results are in no way inconsistent, I decided to repeat a part of the work, in order to obtain a more certain estimate of the various temperatures corresponding to the varying conditions of the cupric oxide. In my previous paper the higher degrees had been merely guessed, for they were not directly concerned in the point then under consideration.

The usual modes of determining high temperatures,—the calorimeter, the air-thermometer, the bolometer, the meldometer, the platinum-iridium thermopile, etc.,—are somewhat troublesome to use for a brief series of experiments of the present kind, so that it seemed best to determine the several temperatures approximately by finding, for each temperature, two substances whose melting-points were respectively above and below the point in question. For instance, an intensity of heat which would melt pure argentic bromide but not pure argentic chloride must be between 427° and 451°, a grade of accuracy more than sufficient for the present purpose.[1] This method of determining the temperature has the great advantage of providing an approximate self-registering thermometer, occupying very small space and needing no connection with

[1] Of course this idea is no new one. It has not often been used so systematically as in the present case, however.

the outside air. The usefulness of the method obviously depends upon the number of substances easily obtained in a pure state, whose melting-points are accurately known. For such knowledge of high melting-points we depend mainly upon four researches,—those of Carnelley,[1] Le Chatelier,[2] Meyer, Riddle, and Lamb,[3] and Ramsay and Eumorfopoulos.[4] Unfortunately the results of these four investigations do not always agree, their disagreement affording evidence of the great difficulty of measuring accurately high temperatures. At first sight the fact of the existence of such discrepancy might deter one from adopting this standard of reference, but further consideration leads to exactly the opposite conclusion. The melting-points of pure salts must be an unchangeable standard, and the uncertainty of our knowledge regarding them must be largely due to experimental difficulties in the thermometric manipulation. These difficulties, if so serious in researches where everything was favorable to accuracy, must be largely augmented in a research like the present one, in which the temperature could not be made the sole issue of the experiment. Hence the melting-point of a pure salt is the safest possible standard. The following table gives in parallel columns the salts chosen for the present scale of temperature, with the results of the four investigations, and the values of the melting-points selected as the most probable.

[1] Carnelley : J. Chem. Soc., **29**, 489, **33**, 273, (1876 and 1878).
[2] Le Chatelier : Bull. Soc. Chim., **47**, 300, (1887).
[3] V. Meyer, Riddle, and Lamb : Ber. d. chem. Ges., **27**, 3129, (1895).
[4] Ramsay and Eumorfopoulos : Phil. Mag., (5) **41**, 360, (1896).

TEMPERATURE SCALE.

	Carnelley calorimeter.	Le Chatelier thermoplle.	Meyer air therm.	Ramsay meldometer.	Value selected.
Potassic	339	...	...	339	339
AgI,2AgBr,2AgCl	383	...	...	...	383
Argentic bromide	427	...	...	426	427
Argentic chloride	451	...	...	460	451
Plumbic chloride	498	...	...	447	498
Argentic iodide	527	...	...	556	529
Sodic biborate	561	...	...	...	561
Lithic chloride	598	...	...	491	598
Thallous sulphate	632	...	...	...	632
Strontic nitrate	645	...	...	570	645(?)
Potassic bromide	699	...	722	733	720
Potassic chloride	734	740	800	762	760
Sodic chloride	772	775	815.4	792	790
Sodic carbonate	814	810	849	851	830
Strontic chloride	825	840	832	796	835 (?)
Sodic sulphate	861	867	863	884	865
Baric chloride	860	...	921	844	920 (?)
Potassic sulphate	...	1045	1078	1052	1060

The most serious discrepancies are to be noticed in the cases of potassic and sodic chlorides, where the respective averages have been chosen as the most probable values. These averages are almost identical with the figures obtained by Ramsay and Eumorfopoulos. On the other hand, Joly's meldometer, used by these investigators, seems to have been much less satisfactory at lower temperatures; for their melting-points of plumbic chloride and lithic chloride are widely different from Carnelley's. Repeated qualitative experiments have convinced me that plumbic chloride is less easy to melt than argentic chloride, and lithic chloride less easy to melt than argentic iodide; therefore Carnelley's calorimetric results have been adopted here as the more accurate. Strontic nitrate, and strontic and baric chloride all begin to decompose in the air at or near their melting-points; undoubtedly this fact is responsible for the very low results obtained by Ramsay and Eumorfopoulos in these cases. Obviously such salts cannot be relied upon as trustworthy thermometers, un-

less one takes the precautions observed by Meyer, Riddle, and Lamb in their work with the air thermometer. One is reminded of the interesting work of Hill upon changeable organic melting-points.[1] The other substances in the list are sufficiently stable, and are easily obtained in a pure state. In the light of Le Chatelier's complete confirmation of Carnelley's results by means of the pyrometric thermopile, it is odd th at the lamented Victor Meyer accorded Carnelley so little credit as he has done.

It is needless to state that pains was taken to eliminate impurities from these substances by recrystallization or other suitable means, and to dry the salts thoroughly, in the work which follows. If the temperature was below 800°, the dry coarsely powdered substances were contained in small melting-tubes of the hardest Jena glass, sealed while hot at both ends, and sometimes provided with a small platinum sinker to show whether or not the salt had liquefied. If, on the other hand, the height of the temperature excluded glass, the substances were contained in small cups beaten into stout strips of platinum foil. The small amount of impurity taken from the glass tubes in which some of the substances were melted could hardly have had much effect on the melting-point until after a considerable mass of the substances had been melted; but then their mission had been fulfilled.

The table above might well be amplified to cover a wider range, as well as smaller differences of temperature, but such an amplification would constitute a research of some magnitude in itself. For present purposes the above will suffice.

Two forms of apparatus were used for determining the amount and the composition of the occluded gases. The first was identical in every respect with the most convenient of the three forms described in the original paper.[2] It consists of several bulbs blown in the bend of a glass tube bent at a right angle. One arm of the tube is temporarily closed by a stopcock (not shown in the cut in the original paper, although mentioned in the letterpress), and in this arm the gas evolved in the bulbs by the solution of the cupric oxide in acid, is collected and measured over boiled water. When necessary the gas

[1] H. B. Hill, Proc. Am. Acad., **23**, 219. [2] Proc. Am. Acad., **26**, 284, (1891).

may be readily removed through the stopcock at the end of the arm; if a gas burette is attached here, of course the gas may be analyzed at once without further trouble.

For most of the experiments, however, Scott's modification of another of the original forms[1] was used. The mode of operating this apparatus was essentially similar to the method just described, although the bent tubes and bulbs are replaced by a small flask and funnel-tube. Scott's addition of a side tube to remove the displaced water distinctly increases the convenience and accuracy of the contrivance. For the details his paper should be consulted.

The two pieces of apparatus give identical results, which cannot be far from the truth. If at all in error the amount of gas collected must be too small rather than too large, for both oxygen and nitrogen are slightly soluble in water. This consideration was verified by fusing a specimen of oxide (another portion of which had been repeatedly analyzed in the usual fashion) with carefully prepared acid potassic sulphate in a Sprengel vacuum. The amount of gas evolved by this treatment was slightly greater, but only slightly greater than the amount obtained by the usual method, and its composition was essentially identical with that of the gas collected over boiled water. Since the question is one of relation, rather than of absolute values, the method involving the use of aqueous solutions was adopted because of its far greater ease of execution. Pains was taken to have the conditions of the solution of the oxide always as nearly as possible the same, so that the results should be strictly comparable with one another.

The first object of the present paper is to show more clearly the relation between the amount of gas retained by the oxide and the temperature used in its ignition. The material employed in these experiments was prepared by dissolving pure copper wire or electrolytic copper in pure nitric acid, and gradually converting by heat the crystallized cupric nitrate, finally into oxide.[2] Platinum vessels were used throughout,

[1] Proc. Am. Acad., **26**, 285, middle of page.

[2] It is interesting to note that the hydrate of cupric nitrate, which crystallizes from hot solutions, probably has the formula $3Cu(NO_3)_2.8H_2O$ (analogous to cadmic sulphate), not $Cu(NO_3)_2.3H_2O$ (Graham), as is usually supposed. Following are the

whenever heating was necessary, excepting that one or two of the first ignitions were conducted in a porcelain boat. Three preparations of the oxide were made; one by the rapid decomposition of the nitrate, another by more gradual application of heat, and a third by the very slow action of a temperature just barely sufficient to effect the desired change. This temperature had been found previously by a special experiment to be about 280°, if the products of the decomposition remain in contact with the cupric oxide. The first of these preparations was the most coherent, and was capable of retaining the most gas; the second was less coherent and retained less gas; and the last was the most powdery and retained even less gas. Thus it is manifest that the physical condition of the solid is a factor in the question.

These specimens of the oxide of copper were subsequently ignited at varying temperatures for varying lengths of time in two different forms of furnace. For the first series a large tube or small muffle of Berlin porcelain capable of being heated to 1200° or more in a Fletcher furnace was used, but since it was found difficult to maintain the tube at a constant temperature throughout, this arrangement was later abandoned. All the subsequent ignitions were performed in a double crucible arranged in the manner shown in the diagram, the low platinum crucible or capsule used to contain the cupric oxide being protected from radiation and convection by a number of superimposed crucible lids. The outer glazed porcelain crucible and the layers of asbestos board covering the draught holes united in excluding the products of com-

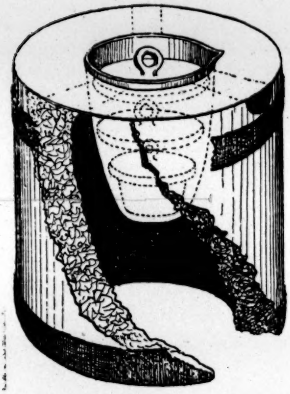
analyses of three separate preparations, dried over moist potash (which does not dehydrate the crystals at ordinary temperatures), proving this point.

(1) 0.1739 gram of crystals yielded 0.0471 gram of copper = 27.08 per cent.
(2) 0.6310 " " " 0.1705 " " " = 27.01 "
(3) 1.2897 " " " 0.3448 " " " = 26.73 "

Average = 26.94 "

Theoretical value for $Cu(NO_3)_2.3H_2O$ = 26.20 per cent. of copper.
" " $3\,Cu(NO_3)_2.8H_2O$ = 26.98 " "
" " $2\,Cu(NO_3)_2.5H_2O$ = 27.35 " "

The crystals analyzed in No. 3 above were large and undoubtedly contained included mother-liquor. Whether or not other hydrates exist, and what the transition temperatures may be, I did not take the trouble to discover. Much of our present data regarding water of crystallization has been rounded off in the manner indicated above. Undoubtedly many more such irregular ratios as 3 : 8 really exist than we are prepared at present to believe.



bustion of the illuminating gas from the contents of the inner capsule. By means of this furnace, fed with a constant gas supply burning from a fourfold Bunsen burner, a surprisingly constant and uniform temperature may be maintained for an indefinite length of time.

In the following table are given the new series of results showing the relation of the total volume of gas retained to the temperature used in the ignition of the cupric oxide. The gas volumes are reduced to 0° and 760 mm. pressure, the reduction having been made by means of a Winkler-Lunge corrector arranged to give directly the exact volume of a mass of moist air which would measure a hundred cubic centimeters when dry and under standard conditions.

THE EFFECT OF TEMPERATURE ON THE TOTAL AMOUNT OF GAS OCCLUDED BY CUPRIC OXIDE.

First Series: First Preparation of Cupric Oxide.

		Cc. gas.
1.	1 gram CuO, heated 1 hour at 300° ±,[1] gave	0.18
2.	1 gram CuO, heated 1 hour at 300° ±, gave	0.19
3.	1 gram CuO, heated 1 hour at 300° ±, gave	0.21
	Average	0.19

[1] Mercury thermometer.

4.	1 gram CuO, heated 4 hours at 500° ±,[1] gave	0.69
5.	1 gram CuO, heated 4 hours at 200° ±, gave	0.72
	Average	0.70
6.	1 gram CuO, heated 1 hour at 830° ±,[2] gave	0.68
7.	1 gram CuO, heated 1 hour at 830° gave	0.69
8.	1 gram CuO, heated 1 hour at 830° gave	0.68
	Average	0.68
9.	1 gram CuO, heated ½ hour at 870° ±,[3] gave	0.55
10.	1 gram CuO, heated ½ hour at 900° ±,[4] gave	0.08
11.	1 gram CuO, heated ½ hour at 950° ±,[5] gave	0.05
12.	1 gram CuO, heated ½ hour at 950° ±, gave	0.04
	Average	0.05
13.	1 gram CuO, heated ½ hour at 1100° ±,[6] gave	0.01(?)

Second Series: Second Preparation of Cupric Oxide.

14.	1 gram CuO, heated 4 hours at 280° ±,[7] gave	0.04
15.	1 gram CuO, heated 1 hour at 290° ±,[7] gave	0.12
16.	1 gram CuO, heated 5 hours at 630°,[8] gave	0.54
17.	1 gram CuO, heated 3 hours at 830°,[9] gave	0.57
18.	1 gram CuO, heated 3 hours at 830°, gave	0.59
19.	1 gram CuO, heated 5 hours at 830°, gave	0.57
	Average	0.58
20.	1 gram CuO, heated 20 minutes at 870° ±,[9] gave	0.42
21.	1 gram CuO, heated 150 minutes at 870° ±, gave	0.23
22.	1 gram CuO, heated 150 minutes at 870° ±, gave	0.14
23.	1 gram CuO, heated 2 hours at 950° ±,[9] gave	0.04
24.	1 gram CuO, heated 2 hours at 950° ±, gave	0.07
25.	1 gram CuO, heated 2 hours at 950° ±, gave	0.04
	Average	0.05

[1] Plumbic chloride just fused: argentic iodide remained solid.

[2] Sodic chloride easily fused; strontic chloride just fused; sodic sulphate remained solid.

[3] Sodic sulphate just fused.

[4] Sodic sulphate easily fused; higher than last.

[5] Baric chloride easily fused; potassic sulphate remained solid.

[6] Potassic sulphate fused, as well as the cupric oxide itself.

[7] Mercury thermometer.

[8] Thallous sulphate just melted.

[9] See foot-notes to preceding series for criteria regarding temperatures 830°, 870° and 950°.

These two series of experiments, qualitatively and quantitatively similar to those carried out in 1891, lead to the following conclusions, which are copied verbatim from the paper on the atomic weight of copper :—

" First, *that cupric oxide prepared by the ignition of the oxy-nitrate after Hampe's method contained between four and five times its volume of occluded gas.*

" Second, *that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was, nevertheless, considerably above that which Hampe apparently employed.*"

The recent experiments add to these conclusions only greater definiteness. It is now clear that nearly all the gas is retained until a temperature of slightly over 850° is reached, when more than 0.9 of it is rapidly set free. Somewhat above this point the cupric oxide is itself partly decomposed ; and in the neighborhood of 1000° the mixture of cupric and cuprous oxides fuses first into a mass resembling scoria, and then into a limpid fluid. It is evident that Scott must have used in his muffle a temperature somewhere between 850° and 1000°, for he found on the average 0.055 cc. of gas per gram of cupric oxide, while my results obtained by means of temperatures in this neighborhood average 0.05 cc. Moreover, some of his material was slightly reduced, but apparently none of it was melted.

It was clearly shown in the previous papers that the low results given by material ignited at temperatures below 450° are due to the presence of undecomposed cupric nitrate, which by its decomposition at higher temperatures yields the gas forming the subject of the present discussion.

The fact that prolonged ignition does not affect the amount of gas occluded may be inferred from the experiments just recorded ; but, in order to obtain more definite information on this influence of time, a third series of experiments was made.

THE EFFECT OF TIME OF IGNITION ON THE TOTAL AMOUNT OF GAS OCCLUDED BY CUPRIC OXIDE.

Temperature: The Fusing-Point of Thallous Sulphate, about 640°.

		Cc. gas.
26.	1 gram of CuO, after ignition for 10 minutes, gave	0.56
27.	1 gram of CuO, after ignition for 10 minutes, gave	0.57
28.	1 gram of CuO, after ignition for 10 minutes, gave	0.53
	Average	0.55
29.	1 gram of CuO, after ignition for 5 hours, gave	0.56
30.	1 gram of CuO, after ignition for 5 hours, gave	0.59
	Average	0.57
31.	1 gram of CuO, after ignition for 20 hours, gave	0.56
32.	1 gram of CuO, after ignition for 20 hours, gave	0.59
	Average	0.57

A portion of the last specimen, which had been heated for twenty hours, was further ignited for five hours at about the fusing-point of common salt (about 800°). Upon solution in acid this portion yielded the same amount, 0.59 cc. of gas. Thus another of the conclusions arrived at in 1892 is confirmed.

"Third, *that beyond a certain limit the time of ignition makes no important difference.*"

This is true, however, only below 850°. Experiments 20 to 22 show that when the imprisoned gas has once begun to be set free, at temperatures above 850°, the time is an essential factor; and that when sufficient time has been allowed, the expulsion of the gas is almost complete. Scott examined only cupric oxide from which he had thus expelled nearly all the gas, hence it is not surprising that he found very little.

In this connection it is interesting to note that Morse and Arbuckle[1] have recently verified, with apparatus far more elaborate and exact than ours, the results of Rogers and myself concerning the amount of gas occluded by the oxide of zinc.[2] Considering the fact that the manner of preparation of

[1] This JOURNAL, **20**, 195. [2] *Ibid.*, **15**, 567.

the substance undoubtedly affects the amount of gas retained, the closeness of the agreement is surprising. Only one of their conclusions is different from ours: in their opinion, there is no reason to believe that the temperature of ignition of the oxide has any effect on the *composition* of the occluded gas, while in our experiments the imprisoned oxygen decreased with increasing temperature. The basis of their reasoning is the supposition that the total amount of gas retained is dependent solely upon the temperature; using this total amount as a thermometer, they point out the fact that the smaller amounts of gas obtained in their experiments did not always contain the smaller amounts of oxygen; and hence they conclude that the temperature is not an essential determining cause of the composition of the mixture. In a letter answering some questions about the matter, Professor Morse kindly writes, "We made every effort to secure constant temperatures for our oxide, giving the closest attention, to that end, to every detail of the firing of the furnace, the fuel, the location of the crucibles," etc. Since this is the case, and I cannot doubt the essential success of their efforts, it seems to me that their results have but little bearing upon the effect of *varying* temperatures on the oxide. The fact that their mixture of gases was by no means constant in composition is better explained by the supposition that some other cause besides the temperature influences the relation of the volumes of oxygen and nitrogen retained, or else that the total amount of the enclosed gases is not a safe measure of the temperature. It will be shown that both of these inferences are correct, and hence that the logic of Morse and Arbuckle's point, correct in itself but unsafe in its premises, falls to the ground.

A careful study of all the data, Morse and Arbuckle's, as well as ours, convinced me that, while the two gases must be evolved together, they behave subsequently in quite a different fashion. It is apparent immediately that the oxygen must escape at first much faster than the nitrogen, for the ratio of the two volumes in the nitric anhydride set free must be originally 5 : 2, while the average of Morse and Arbuckle's result showed that less than a fifth of the finally retained mixture consisted of oxygen. Part of the loss might be due to

the preliminary formation of lower oxides, and to unequal diffusion, but this cannot account for so great a loss of oxygen. Even nitrous oxide should yield upon decomposition a mixture one-third of the volume of which must consist of oxygen; and the fractional diffusion of this mechanically enclosed mixture should allow the lighter of its two constituents, nitrogen, to escape the more quickly of the two; hence, the mixture should contain never less than thirty-three per cent. of oxygen. The same anomaly is even more manifest in the case of cupric oxide, for from this substance nearly all the oxygen soon escapes, even at comparatively low temperatures.

Why then does the oxygen escape the more easily of the two gases? This question introduces us at once to the second section of the paper, which deals with the composition of the occluded gases.

The first step toward answering the question is a certain determination of the facts, which have been doubted by Morse and Arbuckle. The three conditions which would be most likely to affect the amount and composition of the gaseous mixture are the temperature of ignition, the time of ignition, and the compactness of the solid material. In order to test the effect of these possible modifying causes experimentally, several series of analyses were made, both with zincic and with cupric oxide.

The zincic oxide was made by heating pure zincic nitrate for a long time at 280°. It was more compact than the cupric oxide, and undoubtedly contained residual traces of nitrate until further ignited.

THE EFFECT OF TEMPERATURE ON THE TOTAL VOLUME OF GAS OCCLUDED BY ZINCIC OXIDE.

First Series: Heated Three Hours.

	Cc. gas.
34. 1 gram of ZnO, after heating 3 hours at 660°±, gave	0.365
35. 1 gram of ZnO, after heating 3 hours at 660°±, gave	0.380
Average	0.373
36. 1 gram of ZnO, after heating 3 hours at 750°±, gave	0.233
37. 1 gram of ZnO, after heating 3 hours at 750°±, gave	0.210
Average	0.221

38. 1 gram of ZnO, after heating 3 hours at 880°±, gave 0.14
39. 1 gram of ZnO, after heating 3 hours at 880°±, gave 0.18

Average 0.16

Second Series: Heated Thirty Minutes.

40. 1 gram of ZnO, after heating ½ hour at 750°±, gave 0.366
41. 1 gram of ZnO, after heating ½ hour at 750°±, gave 0.320

Average 0.343

42. 1 gram of ZnO, after heating ½ hour at 880°±, gave 0.192
43. 1 gram of ZnO, after heating ½ hour at 880°±, gave 0.192

Average 0.192

Evidently, other conditions being equal, the total amount of gas retained decreases very considerably as the temperature of ignition is raised. Each one of these specimens of gas was analyzed, by means of Hempel's apparatus modified for use on a small scale,[1] with interesting results. The actual volume of *nitrogen* in every gram of material was found to be

FIGURE 2.

almost identical, diminishing only very slightly, if at all, as the temperature increased, and amounting to about 0.14 cc. Thus the large differences in the total volumes are due almost wholly to *oxygen*, which varied from over 60 per cent. in the first average, to less than 20 per cent. in the third. The small amount of carbon dioxide present was absorbed almost completely by the boiled water over which the gases were collected, hence it need not be considered.[2] The actual volumes of nitrogen in the five averages were respectively 0.138, 0.133, 0.130, in the first series, and 0.152 and 0.127 in the second series, while the actual amounts of oxygen were re-

[1] The most important modification was the arrangement for connecting pipette to burette. By blowing and drawing down the capillary it may be made to fit so perfectly into the fine rubber tube as to make the loss of small bubbles impossible. The diagram will make the idea clear (Fig. 2).

[2] This JOURNAL, 15, 572. In a number of cases where pains was taken to measure the carbon dioxide, its volume never exceeded 3 or 4 per cent., and was usually about 2 per cent.

spectively 0.235, 0.087, 0.030 in the first series, and 0.191 and 0.065 in the second. No better proof could be desired of the fact that zincic oxide allows its oxygen to depart more easily than its nitrogen. These results are wholly confirmatory of the results of Richards and Rogers, already mentioned; but, of course, they do not explain how Morse and Arbuckle, working at nearly constant temperature, obtained inconstant results. To accomplish this explanation, the other possible causes affecting the retention of gases must be considered.

THE EFFECT OF TIME OF IGNITION ON THE AMOUNT OF GAS RETAINED BY ZINCIC ACID.

First Series: Just above the Melting-point of Thallous Sulphate.

	Cc. gas.
44. 1 gram of ZnO, heated at **660°** for **1** hour, gave	0.46
34. 1 gram of ZnO, heated at **660°** for **3** hours, gave	0.36
35. 1 gram of ZnO, heated at **660°** for **3** hours, gave	0.38
Average	0.37

Second Series: Just above the Melting-point of Potassic Chloride.

45. 1 gram of ZnO, heated at **750°** for **10** minutes, gave	0.27
46. 1 gram of ZnO, heated at **750°** for **20** minutes, gave	0.35
40. 1 gram of ZnO, heated at **750°** for **30** minutes, gave	0.37
41. 1 gram of ZnO, heated at **750°** for **30** minutes, gave	0.32
Average	0.35
47. 1 gram of ZnO, neated at **750°** for **60** minutes, gave	0.30
48. 1 gram of ZnO, heated at **750°** for **60** minutes, gave	0.32
Average	0.31
36. 1 gram of ZnO, heated at **750°** for **180** minutes, gave	0.21
37. 1 gram of ZnO, heated at **750°** for **180** minutes, gave	0.25
Average	0.23

Third Series: Just above the Melting-point of Sodic Sulphate.

49. 1 gram of ZnO, heated at **880°** for **3** minutes, gave	0.49
50. 1 gram of ZnO, heated at **880°** for **5** minutes, gave	0.35
51. 1 gram of ZnO, heated at **880°** for **12** minutes, gave	0.29
52. 1 gram of ZnO, heated at **880°** for **12** minutes, gave	0.25
Average	0.27

42. 1 gram of ZnO, heated at 880° for 30 minutes, gave 0.19
43. 1 gram of ZnO, heated at 880° for 30 minutes, gave 0.19

Average 0.19

38. 1 gram of ZnO, heated at 880° for 180 minutes, gave 0.14
39. 1 gram of ZnO, heated at 880° for 180 minutes, gave 0.18

Average 0.16

In each of the series the same fact may be noted—the fact that continued heating at any one temperature is capable of causing a slow evolution of gas from the oxide. Only in the second of these series is evident an initial increase in the amount of gas, indicating a maximum after less than twenty minutes of heating. This increase, which is manifestly due to the advancing decomposition of the traces of imprisoned nitrate, undoubtedly ceases after an hour's heating at 660°, or after three minutes' heating at 880° ; hence it does not appear in the first and third series.

The steady loss of gas after this maximum has been attained—a loss increasing with time as well as with increasing temperature in the case of *zincic* oxide—is worthy of further attention, especially because it will be remembered that the amount of gas retained by *cupric* oxide remained almost constant until a very high temperature was reached. Analysis of the several specimens of gas showed at once wherein lay the explanation ; for they showed as before that the maximal quantities of gas consisted chiefly of oxygen ; while the gas obtained by the last two experiments consisted chiefly of nitrogen. Here, again, the nitrogen remained nearly constant, only diminishing from 0.20 cc. at the maxima to about 0.13 cc. at the minima , while the oxygen diminished in the same samples from 0.21 to 0.03 cc.

It remains only, as far as zincic oxide is concerned, to show how wide a difference in the amount of gas may be caused by the original mode of preparation of the solid material.

THE EFFECT OF PHYSICAL CONDITION UPON THE TOTAL AMOUNT OF GAS RETAINED BY ZINCIC OXIDE.

	Cc. gas.
53. 1 gram of ZnO, prepared from zincic carbonate at 880°, gave	0.00
54. 1 gram of ZnO, prepared from zincic carbonate at 880°, gave	0.00
Average	0.00
55. 1 gram of ZnO, prepared from the nitrate at 280°, not ignited, gave	0.01
56. A similar experiment gave	0.02
Average	0.015
57. 1 gram of ZnO, prepared from zincic nitrate, but heated to 880° in a slightly reducing atmosphere, gave	0.05
58. A similar experiment gave	0.15
Average	0.10
42. 1 gram of ZnO, prepared by gentle heating of the nitrate at 280°, and subsequent ignition for 30 minutes at 880° in an oxidizing atmosphere, gave	0.192
43. A similar experiment gave	0.192
Average	0.192
59. 1 gram of similar ZnO, prepared in the same way, but heated to 670° for 3 hours and then preserved two weeks before heating ½ hour at 880°, gave	0.292
60. A similar experiment gave	0.260
Average	0.276
61. 1 gram of more compact ZnO, prepared by heating the nitrate rapidly, and having been preserved for two weeks before being ignited for ½ hour at 880°, gave	0.387
62. A similar experiment gave	0.396
Average	0.392

The evidence of these results proves that the total amount of gas retained by zincic oxide varies with every detail of the method of preparation; hence this amount cannot serve as a sure guide to the temperature of ignition, unless a perfectly

uniform sample is used for all trials.[1] Of course the amounts of nitrogen found in these samples varied widely; for the gas resulted from the decomposition of zincic nitrate, which was imprisoned in varying quantities according to the physical condition of the zincic oxide.

Since so many circumstances regulate both the amount of gas and its composition, one is not surprised that Morse and Arbuckle obtained varying mixtures with eight different preparations of zincic oxide. It is true that their expulsion of the gases continued until it had become so slow that two successive weighings with intermediate heating gave constant weight; but the same causes of change must still have been at work, although far more slowly.

In the light of these interesting results, it seemed worth while to make a more elaborate investigation of the relation the composition of the gases held by *cupric* oxide to the temperature used in its ignition. The material used in the following determinations was the soft powder made by the decomposition of cupric nitrate at 280°.

THE EFFECT OF TEMPERATURE OF IGNITION ON THE COMPOSITION OF GASES RETAINED BY CUPRIC OXIDE.

Time of Ignition, 1 Hour.

	Per cent. oxygen.
63. 0 32 cc. gas from 1 gram CuO heated at 520° contained	18
64. 0.34 cc. gas from 1 gram CuO heated at 520° contained	15
Average	16.5
65. 0.49 cc. gas from 1 gram CuO heated at 660° contained	6
66. 0.48 cc. gas from 1 gram CuO heated at 660° contained	5
	5.5
67. 0.47 cc. gas from 1 gram CuO heated at 750° contained	3
0.47 cc. gas from 1 gram CuO heated at 750° contained	4
Average	3.5

[1] Small quantities of such impurities as alkali and silica do not seem to affect the occlusion, however. See THIS JOURNAL, 15, 574.

0.05 cc. gas from 1 gram CuO heated at 1000° ± contained 0 to 4 per cent. oxygen according to Alexander Scott.

It is evident that the cupric nitrate remaining in the cupric oxide had not been wholly decomposed by heating for an hour at 520° (experiments No. 63 and 64) and that we are dealing here with an increasing total, and a maximum similar in every respect to that already noted in the case of zinc,[1] except that in the present case more nitrogen is held, while the oxygen escapes at a much lower temperature.

THE EFFECT OF TIME ON THE COMPOSITION OF THE GAS RETAINED BY CUPRIC OXIDE.

First Series: Temperature, 500°.

(Argentic chloride easily melted; plumbic chloride scarcely melted.)

	Per cent. oxygen.
68. 0.29 cc. gas from 1 gram CuO heated 2 hours contained	25
69. 0.29 cc. gas from 1 gram CuO heated 2 hours contained	23
Average	24
70. 0.38 cc. gas from 1 gram CuO heated 8 hours contained	15
71. 0.42 cc. gas from 1 gram CuO heated 8 hours contained	14
Average	14.5
72. 0.46 cc. gas from 1 gram CuO heated 16 hours contained	8

Second Series: Temperature, 520°.

(Just below the melting-point of argentic iodide, but distinctly above that employed in the last series.)

73. 0.15 cc. gas from 1 gram CuO heated for 15 minutes contained	23
63. 0.32 cc. gas from 1 gram CuO heated for 1 hour contained	18
64. 0.34 cc. gas from 1 gram CuO heated for 1 hour contained	15

[1] See page 716.

74. 0.48 cc. gas from 1 gram CuO heated for 2 hours contained **12**
75. 0.49 cc. gas from 1 gram CuO heated for 16 hours contained **6**

Third Series. Temperature, 600°.

(Argentic iodide fused easily; lithic chloride fused slowly.)

76. 0.43 cc. gas from 1 gram CuO heated for 10 minutes contained **12**
77. 0.38 cc. gas from 1 gram CuO heated for 10 minutes contained **12**

Average **12**

78. 0.46 cc. gas from 1 gram CuO heated for 20 minutes contained **13**
79. 0.53 cc. gas from 1 gram CuO heated for 35 minutes contained **10**
80. 0.51 cc. gas from 1 gram CuO heated for 35 minutes contained **8**

Average **9**

Fourth Series: Temperature, 640°.

(Thallous sulphate just fused; strontic nitrate remained solid).

81. 0.21 cc. gas from 1 gram CuO heated for 2 minutes contained **35**
82. 0.19 cc. gas from 1 gram CuO heated for 2 minutes contained **36**

Average **35.5**

83. 0.43 cc. gas from 1 gram CuO heated for 10 minutes contained **19**
84. 0.45 cc. gas from 1 gram CuO heated for 10 minutes contained **16**

Average **17.5**

85. 0.46 cc. gas from 1 gram CuO heated for 8 hours contained **6**
86. 0.45 cc. gas from 1 gram CuO heated for 8 hours contained **4**

Average **5**

It is clear that we are dealing here with a phenomenon precisely similar to that observed in the case of zinc. The decomposition of the remaining traces of nitric anhydride takes place much more slowly at low temperatures than at high ones, and the oxygen formed by this decomposition is liberated far more rapidly during the hotter ignitions.

A single series of experiments,[1] made some years ago with magnesic oxide, showed that this substance too acted in the same way, and it is probable that all the other oxides retaining traces of occluded gases would give similar results. The data obtained from magnesic oxide are repeated below, in order that all the facts may be at hand for the following consideration of the causes of the anomaly.

GAS EVOLVED FROM MAGNESIC OXIDE.

(*Temperature of Ignition was about* 700°–800°.)

1 gram MgO after ignition 30 minutes gave 3.60 cc. nitrogen and 7.2 cc. oxygen.

1 gram MgO after ignition 60 minutes gave 4.72 cc. nitrogen and 6.3 cc. oxygen.

1 gram MgO after ignition 75 minutes gave 4.84 cc. nitrogen and 4.4 cc. oxygen.

1 gram MgO after ignition 135 minutes gave 5.44 cc. nitrogen and 3.6 cc. oxygen.

1 gram MgO after ignition 195 minutes gave 5.24 cc. nitrogen and 2.8 cc. oxygen.

HYPOTHETICAL EXPLANATION.

The facts are now perfectly clear, and it remains only to account for them by means of a plausible theory. In the first place there can be no question that the gases proceed from a residue of basic nitrate imprisoned in the oxides in question; the fact that oxides prepared from the carbonates contain little or no gas would alone be sufficient support for this point of view. The first matter to be considered is, then, the dissociation of this residual nitrate, which is probably wholly analogous to that of calcic carbonate as studied by Le Chatelier.[2] We may express this reaction, perhaps, in the follow-

[1] This JOURNAL, **15**, 576.

[2] Compt. rend., **102**, 1243 (1886). Nernst: Theor. Chem., p. 377 (1894).

ing fashion, which indicates that the proceeding is supposed to take place in the gaseous phase, while the solids enter into the reaction solely by their vapor-tension :

$$\underset{\text{Vapor.}}{Cu(NO_3)_2.3CuO} \rightleftarrows \underset{\text{Vapor.}}{4CuO} + [N_2O_5]$$

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$\underset{\text{Solid.}}{Cu(NO_3)_2.3CuO} \qquad \underset{\text{Solid.}}{4CuO}$$

It is probable that Graham's basic cupric nitrate $Cu(NO_3)_2.3Cu(OH)_2$ is dehydrated before the nitric acid begins to leave ; if it is not, of course three molecules of water must be added to the products above.[1] The gaseous products of this reaction attain the atmospheric pressure at about 280°.

The reaction represented above is evidently only a preliminary stage of the whole change ; it may have scarcely begun, or may have run almost to an end in some cases before the dissociation of the nitric anhydride begins to enter into the problem. This dissociation may be complete, resulting in a mixture of the elementary gases, or it may (and does at ordinary pressures) stop at one of the lower oxides of nitrogen. Since the gases, whatever they may be, are necessarily held in microscopic cells, while their own volume under ordinary pressure is several times that of the total volume of the solid containing them, it is obvious that the pressure under which they exist must be very great. At this great pressure the stability of N_2O_5 must be very considerably increased, for the reaction $2N_2O_5 = 2N_2 + 5O_2$ is one which pressure must seriously affect because of the change of volume concerned in it ; but more probably the peroxide of nitrogen is the first product of the reaction. In any event, it is evident that the complete separation of the oxygen and nitrogen does not take place immediately, for much less nitrogen was yielded by the specimens of each oxide heated for a short time at comparatively low temperatures than by like specimens heated longer or hotter.

[1] This conclusion is based upon the fact that no water is to be found after the ignition is completed (Proc. Am. Acad., **26**, 278). The presence of water would not affect the general tendency of the logic concerning the escape of the oxygen and nitrogen ; if, however, it actually remains until the nitrogen compounds have been split up, we must explain its final escape by a double-acting process similar to that used to explain the escape of the oxygen.

Both of these reactions, the decomposition of the cupric nitrate as well as that of the oxides of nitrogen, evidently then require time for their completion, so that the maximum of gas contents is not immediately attained. Besides being accelerated by heat they are also possibly both hastened by the escape of a portion of the oxygen, an interesting phenomenon which occurs side by side with the decomposition. To make the matter clearer, let us represent the dissociation of the oxide of nitrogen by the general formula

$$2NO_x = N_2 + xO_2.$$

The speed of this reaction is represented by the equation

$$-\frac{dc}{d(time)} = kc^2 - k^1 c_1 c_2^x,$$

an expression which increases in magnitude as c_2 (the concentration of the oxygen) diminishes. Since it is probable that k^1 is very small,—that the chief tendency of the reaction is from left to right,—this cause of acceleration is not an important one. In a similar way the decomposition of the oxides of nitrogen likewise accelerates the more complex reaction into which the solids enter.

In every case this decomposition of the oxides of nitrogen, and therefore that of the cupric nitrate, had nearly advanced to completion before the oxygen had all been expelled. This led to the existence of a maximum of gas volume after a brief heating, a maximum less marked in the case of cupric oxide than in the other cases because the extra oxygen escapes from cupric oxide almost as fast as it is formed. Thus many of the apparent eccentricities in the behavior of the gases find a simple and adequate explanation. The numerous results with different oxides were sought in the hope that the relations might be capable of quantitative proof according to the law of mass action, as well as of qualitative demonstration, but the great number of possible compounds and reactions made this hope vain.

It remains only to devise an hypothesis to explain perhaps the most interesting phenomenon under discussion, to show why the oxygen is capable of escaping more rapidly than the nitrogen. Obviously diffusion or transpiration cannot account

for this; for any orifice, no matter how small, which would allow the oxygen to escape, must also allow the nitrogen to escape. The only possible explanation is the supposition that the oxygen finds its way out chemically, by uniting with metal or a lower oxide which has momentarily released some of its proper supply of oxygen. The displaced gas, being forced to find another berth, presently in its turn occupies the place of still another portion, and so on, until most or all of the excess has found its way out of prison. Of course the nitrogen cannot use this means of escape, for it is not surrounded by a compound which yields it upon dissociation; the nitrogen can only escape through holes originally present or formed by the rearrangement ot the substance of the solid.

This hypothesis suggests Grotthus's obsolete explanation of electrolysis, or rather that of Clausius; for the most plausible conception is that in the hot rapidly vibrating solid a portion of the oxygen which ought to be combined with the metal is always in a free state, and that this condition, by a recurring process of dissociation and association, permits relieving the high pressure of the oxygen in the cell. It is possible that water occluded in the oxide may play the part of a go-between, but there is no experimental evidence of this.[1] It is no new idea to explain the diffusion of hydrogen through palladium, or of carbon through iron in the cementation process and other similar phenomena, by a similar mechanical conception.

Quite in accord with this point of view are a number of facts. In the first place cupric oxide, the most easily reducible of the oxides investigated, parts with its occluded oxygen with the greatest ease, at the same time obstinately retaining the nitrogen. The progressive increase in the tendency to retain oxygen in the cases of zinc and magnesium corresponds to the increase in the difficulty of reducing these oxides. In other words, the least stable oxide is the one which has the feeblest hold upon the occluded oxygen. Cupric oxide begins to lose this impurity with great rapidity at 520°, zincic oxide loses it less rapidly even at 750°, and magnesic oxide is still more obstinate. It is probable, more-

[1] See foot note on p. 722.

over, that in the cases of zinc and magnesium there is a slight amount of transpiration, for a small part of the nitrogen was found to leave at the higher temperatures. This transpiration ought to assist the oxygen also to escape, although in somewhat less measure than the nitrogen; but in spite of this possibility of more rapid escape, the oxygen is still held more firmly than in the case of cupric oxide. In this latter substance all the *nitrogen* is retained indefinitely at temperatures below 850°, forming the constant gas residue noted in the first experiments; only when the definite structure of the oxide is broken up, and the dissociation tension of the cupric oxide becomes so great that cuprous oxide begins to be formed, does the nitrogen take its flight. On the other hand a reducing atmosphere is needed to force zincic oxide to relinquish all its gas, unless an excessively high temperature is employed. Forty-three years ago Sainte-Claire Deville and Rivot showed that at a red heat such an equilibrium exists between zincic oxide, zinc, hydrogen, and water as to enable zinc oxide to be sublimed in a current of hydrogen, the dissociated oxide reforming when cooled.[1] This reaction undoubtedly enables the occluded gas to escape by destroying the structure of the solid when gases from the flame are present. (Experiments 57 and 58.)

Again, the fact that many solids, the oxides in question among them, manifest upon heating the peculiar contraction called "sintering," is evidence of the existence of molecular instability and possibility of rearrangement. The hypothesis of partial dissociation at high temperatures is adequate to explain this.

It is obvious that the oxide, if it is really dissociated, should be capable of conducting electricity, because of the presence of traces of metal. In order to test this point, small platinum electrodes of 0.25 square centimeter in area and separated from one another by about 0.5 cm., were packed in pure specimens of the several oxides. Each porcelain crucible containing an oxide was gradually heated, after having placed the two electrodes in a circuit with a delicate amperemeter and four accumulators. When cold, the resistence of

[1] Ann. chim. phys. (3), **43**, 7, 476.

each of the oxides was at least 200,000 ohms. Upon heating, the cupric oxide began sensibly to conduct below a red heat, and at about 650° offered only about as much hindrance to the current as was afforded by 550 ohms, remaining constant at that point. On the other hand, zincic oxide fell in resistance only to about 15,000 ohms at 650°, and required fully 900° to bring it as low as 1,000 ohms; while the highest heat of the blast-lamp could not cause the magnesic oxide to transmit as much as the twentieth of a milliampere, the least current capable of being observed upon the amperemeter. It is needless to say that any possibility of the presence of a reducing atmosphere was excluded, and the fact that each oxide returned almost if not quite to its non-conducting state after cooling, is sufficient proof that the heat alone was the cause of the phenomena observed. These interesting results are fully in accord with the hypothesis that cupric oxide is slightly dissociated at a red heat, that zincic oxide is less dissociated, and that magnesic oxide, retaining its occluded oxygen with great obstinacy, is scarcely dissociated at all. Magnesic oxide, being one of the stablest of all compounds at high temperatures, could not be expected to show any appreciable dissociation or conductivity; and the wonder is, that the occluded gas is able to escape even as fast as it does.

This assumed partial thermal dissociation of solids must not be confounded with electrolytic dissociation (ionization); for the energy which determines the separation of the components in the present case is heat, and not electricity. The conductivity is not electrolytic conductivity, but only the metallic conductivity of the metal set free by a purely thermal dissociation. In order to prove this, a current of twenty milliamperes was transmitted through cupric oxide for three hours. This quantity of electricity would have carried nearly seventy milligrams of copper from a cupric solution, and since neither copper nor an oxide appeared adhering to the platinum negative electrode, it is safe to infer that the conductivity is not electrolytic. While these oxides thus conduct electricity without transference of material, it is undoubtedly true that many substances, even glass, for example, which are non-conductors when cold, become capable of carrying a cur-

rent *electrolytically* when heated. Melted salts are well known to be good electrolytic conductors, and Graetz[1] has found that this conductivity begins before the salts have melted. Our knowledge of the rationale of these facts is altogether too incomplete to afford a satisfactory explanation of all the phenomena attending the passage of electricity through solids, liquids, or gases at high temperatures; and it is perhaps unsafe to record the conductivity of cupric oxide as a definite indication of the temporary presence of metallic copper in the case under discussion.

Following is a more certain proof that this dissociation is to be considered as analogous to the decomposition of limestone by heat. Here, as there, the gas, in the present case oxygen, must have a definite pressure of dissociation; but no appreciable amount of metal or lower oxide can form when the tension of the oxygen in the surrounding atmosphere is greater than this definite pressure. On the other hand, cupric oxide should not lose only its occluded oxygen, but all the oxygen that normally belongs to it, leaving metallic copper (or at least cuprous oxide), when heated in a perfect vacuum or in an inert atmosphere, if the hypothesis under consideration is tenable. This decomposition begins even in the air at about 1,000°. The search in chemical literature revealed a statement by Hilditch that cupric oxide ignited at lower temperatures in a vacuum weighs less than it did before, as well as one by Morley, that the same substance slowly evolves a gas when heated in a vacuum.[2] Since it is hard to tell whether this evolution might not be merely that of the occluded gases, it was thought worth while to repeat the experiment.

Two grams of cupric oxide, which had been ignited for a long time in pure air until constant in weight, were found to evolve a gas steadily when heated in a vacuum to about the melting-point of common salt (790°), provided that the gas was removed by a Sprengel pump as fast as it was formed. When allowed to attain equilibrium, this gas (which repeated analysis showed to be almost pure oxygen containing only traces of

[1] Wied. Ann., **40**, 18 (1890).

[2] Hilditch: Chem. News, **49**, 37 (1884). Morley: Am. J. Sci., **41**, 231 (1891).

nitrogen and carbon dioxide) was found to possess a tension of two or three-tenths of a millimeter of mercury. A portion of the same material was heated for many hours more in a crucible to a full red heat; but upon subsequently heating it in a vacuum the evolution of gas proceeded just as before. Since all the occluded oxygen except two or three per cent. had been expelled by the preliminary heating, this must have been structural oxygen. The conclusion was confirmed by the discovery of red cuprous oxide in the residue. Repetitions of the experiment showed that the tension of the gas increased enormously with the temperature, exceeding a millimeter before the glass became so soft as to collapse. In some of the experiments the best Bohemian glass was used, in others the hardest made in Jena. The nature of the glass seemed to be without influence on the result. The amount of gas evolved in a given time naturally depends upon the efficiency of the pump, as well as upon the temperature; in one of the experiments two cc. of oxygen were obtained in eight hours.

Ignition of the substance in an inert atmosphere should produce the same effect. Since cupric oxide is slightly dissociated by heat, perceptible amounts of oxygen should be removed by heating it in nitrogen, just as carbonic acid is removed from limestone by heating it in a current of air. This dissociation of cupric oxide must have its effect on any process involving the ignition of cupric oxide in a vacuum or in an inert gas. The determination of organic nitrogen by means of the Sprengel pump, for example, must be affected by it. The use of carbon dioxide as a displacing medium in the Dumas method, probably disposes of the error, however; for carbon dioxide is itself dissociated by heat, and it undoubtedly furnishes enough oxygen to diminish greatly the decomposition of the cupric oxide.

In the light of these results, it is obviously advisable, when one desires to remove oxygen from a mixture of gases by means of hot copper, to maintain the last portion of the tube at a comparatively low temperature. Even then the issuing gas may not be absolutely free from oxygen.

Every one knows that auric oxide is excessively unstable,

and that argentic oxide is completely decomposed even in an atmosphere of pure oxygen at comparatively low temperatures. The present results merely extend this behavior, in a much smaller degree, to cupric oxide, and the hypothesis carries the idea still further. The dissociation of zincic oxide must of course be yet less, while the tension of oxygen above magnesic oxide even at high temperatures must be an infinitesimal far less in value than the tension of the gas in the vacuum needed for the production of X-rays.

According to the phase rule and the law of mass action these reactions must take place in the gaseous phase,—the only one present of variable composition. As an example, the case of copper is given below :—

$$\begin{array}{ccccc} 4\,CuO & \rightleftarrows & 2\,Cu_2O & + & O_2 \\ \text{Vapor.} & & \text{Vapor.} & & \text{Gas.} \\ \uparrow\downarrow & & \uparrow\downarrow & & \\ 4\,CuO & & 2\,Cu_2O & & \\ \text{Solid.} & & \text{Solid.} & & \end{array}$$

The occluded oxygen is supposed to escape by the oscillation, backward and forward, of this heterogeneous reaction. The ability of the system to be first dissociated and then associated in another place where more oxygen is present presupposes, however, great internal activity in the substance of the hot solids : and this internal activity is the most interesting conclusion to be drawn from the phenomena under discussion.

In short, no matter what point of view one adopts, or what mechanical picture one forms of the reaction, the necessity of ascribing the rapid escape of the oxygen to internal rearrangement seems to be inevitable.

Morse and Arbuckle, in the course of some admirable work upon the atomic weight of cadmium which they have just completed,[1] had occasion to measure the gases occluded by cadmic oxide made from the nitrate. As one would expect, this oxide holds its occluded oxygen more firmly than copper, but less firmly than zinc. In fact, the behavior of the substance, according to Morse and Arbuckle's description, probably accords well with the hypothesis under consideration. The fact that Rogers and I found

[1] This JOURNAL, **20**, 536.

no gas in our cadmic oxide in 1892 is easily accounted for by the circumstance that we used a bright red heat in the ignition, the oxide parting with both gases by the disintegration of its original structure as the oxide of copper did with Scott. Since cadmium is volatile at high temperatures, however, it was natural that its dissociated oxide should have a wider opportunity of rearrangement than in the case of copper; and hence the crystalline structure of the ignited oxide observed in 1892. The volatility of cadmium explains the sublimation of the oxide observed by Morse and Arbuckle; this sublimation was really a dissociation and recombination like the sublimation of sal ammoniac.

Nickel, another metal whose oxide was investigated by Rogers, probably occupies its expected place near cadmium, as far as its oxide's capacity to retain oxygen is concerned. In some recent experiments in this laboratory, Cushman succeeded in partially decomposing nickelous oxide in a stream of nitrogen below 1200°. All these considerations are concordant with the hypothesis devised to explain the escape of occluded oxygen from metallic oxides.

The only point regarding this occlusion of gases left unexplained is the fact that in the experiments of Morse and Arbuckle the total amount of gas was in every case nearly the same, although the proportion of oxygen and nitrogen varied. This is a very interesting circumstance. The experimenters ignited their oxide to constant weight, in other words, until two successive ignitions caused no appreciable change; but it does not follow from this that the evolution of gas had ceased,—one can only maintain that it had become so slow as to be inappreciable. Evidently, then, the question to be answered is,—Why has the oxygen more difficulty in escaping when a small amount of nitrogen is present than when a large amount is present? The reason of this eccentricity may be because those specimens which contain the most gas are naturally the most porous and loosely held together, although usually formed in larger individual aggregations; and the freer atomic and molecular motion allowed by the looser structure may permit the oxygen to leave more rapidly. Hence

in each case the sum of the oxygen and nitrogen amounted to about the same volume. This hypothesis within an hypothesis is rather too uncertain to deserve much emphasis, however.[1]

In the course of some of my old experiments on the impurities in cupric oxide, it became necessary to reduce the substance in a current of carbon monoxide. Referring to this work, Scott, in the paper already cited,[2] expresses surprise at the existence of an admixture of hydrogen in this gas. His experience agrees with that of Stas in finding only a small amount of such gaseous impurity in carbonic oxide obtained from oxalic acid, while my results indicated a large amount. Lord Rayleigh, in the course of his recent valuable work on the density of gases,[3] concludes that his carbonic oxide also was free from hydrogen or hydrocarbons; and indeed there is no reason why this result should not be easily attained if one uses pure materials. Lord Rayleigh explains the existence of hydrogen in my carbonic oxide by drawing attention to the fact that in my case the gas, dried only by calcic chloride, was passed over red hot platinum sponge.

This explanation is undoubtedly correct. Many experimenters have shown that the reaction $CO + H_2O = H_2 + CO_2$ is one easily reversible at high temperatures,[4] and in the presence of a large excess of carbon monoxide, it is obvious that nearly all of the trace of aqueous vapor would be reduced. For my purpose at the time, the source of the hydrogen was of no importance; it was only necessary to know the exact amount of the impurity, and this was suitably determined. It is satisfactory to know the cause of the discrepancy, however, as well as to know that it is easier to prepare carbon

[1] In this connection it is a matter of interest to note that Ramsay (Phil. Mag. [5] **38**, 206, (1894)) has found that the presence of nitrogen in a palladium bulb seems to prevent, to some extent, the diffusion of hydrogen into it. This observation is not unlike Morse and Arbuckle's; but if as a matter of fact an indifferent gas can produce such an effect, our present notions concerning semipermeable septa demand some revision.

[2] *Loc. cit.*, p. 563.

[3] Proc. Roy. Soc., **42**, 204, (1898).

[4] Bunsen: Ann. Chem. (Liebig), **85**, 137 (1853). Horstmann: *Ibid.*, **190**, 228 (1878). Bötsch: *Ibid.*, **210**, 207. And especially Hoitsema: Ztschr. phys. Chem., **25**, 668, as well as others.

monoxide almost free from hydrogen than seriously contaminated with it. More often than we suspect, perhaps, are our carelessly planned efforts at purification apt thus to introduce more impurity than they eliminate.

In a recent number of the Journal of the American Chemical Society (March, 1898), F. R. M. Hitchcock has published a preliminary paper upon the occlusion of various gases by the oxides of the metals, having apparently overlooked the Harvard investigations. It is satisfactory to see the phenomenon widely recognized; for an appreciation of this serious cause of possible constant error will result in the publication of fewer erroneous determinations of atomic weights than have appeared in the past. One should also bear in mind the fact that nitric acid is not by any means the only substance which is liable to leave appreciable contamination in material from which it has been expelled by heat. The number of such occlusions is far greater than most analysts imagine; this fact is not realized because the minute residues are often so hard to detect.

The evidence of this paper proves that in reality no discrepancy exists between the results of Scott, and Morse and Arbuckle, and those obtained at Harvard. The apparent disagreements were caused by the fact that the later experimenters investigated parts only of the wide field outlined in 1892, the relation of the parts to the whole being not wholly realized. The paper also shows that the unequal escape of oxygen and nitrogen imprisoned in the oxides of metals is a phenomenon of great interest, capable of shedding light on the internal kinetics of solids.

CAMBRIDGE, May 1, 1898.

NEW EXPERIMENTS ON THE QUANTITATIVE SYNTHESIS OF WATER.

By Edward H. Keiser.

In the complete syntheses of water made in recent years for the purpose of determining the relative atomic weights of oxygen and hydrogen, the apparatus has been so constructed that the hydrogen was burnt at a jet in an atmosphere of oxygen. When the gases are combined in this way it is found that towards the end of the experiment it is difficult to keep up the combustion, the flame gradually dies out, and finally a residual gas remains in the combustion chamber, consisting of unburnt hydrogen and oxygen and whatever impurities were present in these gases. This residual gas volume must then be pumped out, measured and subjected to eudiometric gas analysis. From the volumes of hydrogen and oxygen thus found the weights of these gases that have remained uncombined must be calculated, and these weights must be deducted from the weights of oxygen and hydrogen found by direct weighing. The final weight of each gas is, therefore, not the result of weighings with the balance, but is dependent upon the accuracy of a volumetric gas analysis involving a number of eudiometric operations and calculations.

With the hope of making a complete quantitative synthesis of water in such a way that the weights of hydrogen, oxygen, and water could be directly determined with the balance, the method described below was devised. It is based upon the fact that hydrogen when occluded in palladium is completely oxidized to water when the palladium hydride is brought in contact with an excess of oxygen.

In outline the steps of the process are as follows: First, a glass vessel with two communicating compartments, one of which is filled with phosphorus pentoxide, is exhausted with an air-pump and weighed. Second, metallic palladium is put into the second compartment, and after exhausting the weight is again determined. Third, pure hydrogen is now admitted, and after the palladium is saturated the vessel is again connected with the air-pump and a portion of the gas is pumped

out and again weighed. The difference between the second and third weighings gives the weight of hydrogen to be oxidized. Fourth, pure oxygen is now slowly admitted, water is formed, and the vessel becomes warm. By regulating the current of oxygen the temperature can be kept down so that it does not rise much above that of surrounding objects. Finally, after all the hydrogen is oxidized and the vessel is full of oxygen, the excess of oxygen is pumped out, the gas, however, in going out is made to pass through the phosphorus pentoxide, so that all water is retained. The vacuous vessel is again weighed. The difference between the third and fourth weighings gives the weight of oxygen that has united with the hydrogen. Fifth, after the palladium has stood in the vacuum over the phosphorus pentoxide and the water has united with the pentoxide, the palladium is removed, and the vessel after exhausting is weighed. The difference between the first and fifth weighings gives the weight of water formed. This weight must agree closely with the sum of the weights of hydrogen and oxygen as previously found, if the experiment is to be regarded as trustworthy.

Fig 2.

Fig. 1.

Fig. 1 shows the construction of the vessel that was used. It consisted of a wide glass tube $5\frac{1}{2}$ cm. in diameter, 19 cm. in length; it was drawn down and closed at the bottom by a narrow tube carrying a glass stop-cock, and at the top by a cap with a three-way stop-cock. The cap was connected with the tube by means of a ground glass joint. The wide tube was constricted as shown in the figure, so as to form two compartments. The lower one served to hold the phosphorus pentoxide, the upper one the palladium. The palla-

dium in the form of sponge was placed in the glass tube shown in Fig. 2. This tube was of such diameter that it could be easily placed inside of the larger tube after the cap had been removed. The constriction prevented it from touching the pentoxide. The dotted lines in Fig. 1 are intended to show the palladium tube in position.

Three tubes of the kind represented in Fig. 1 were made of the same kind of glass and of as nearly equal dimensions as possible. The volume of each was determined by hydrostatic weighing. The volumes of the smaller ones were made as nearly equal as possible to that of the larger one by adding compensating bulbs. Two of the tubes served as counterpoises to the working tube, one to counterpoise it for the first and fifth weighings, when the working tube contained no palladium, the other for the second, third, and fourth weighings, when both palladium and pentoxide were present. Lead in the form of shot was put into the counterpoise tubes until they were somewhat heavier than the working tube. In all the weighings it was, therefore, necessary to add to the scale-pan carrying the working tube but few weights, and these were of small value. The correction of the weights for air displaced was very small, and as the weights of hydrogen and oxygen were not large, the reduction of these weights to a vacuum only affected the ratio in the fourth decimal place, which was within the limits of experimental error.

A Troemner balance with aluminium beam, having a capacity of 250 grams on each scale pan, was used. The method of weighing by reversals was used in all the determinations. With the working tube and the weights on one side, the counterpoise on the other, the fractions of milligrams were found by means of the vibrations and the sensibility. Then the loads were reversed and the weight found in the same way. The mean of the values was taken as the result of one weighing. At intervals of twelve hours the weighing was repeated. If there had been any appreciable leakage of air into the tube, it would have been possible to detect it in this way. The final value for a weight was thus the result of at least two, and in some cases of three and four double weighings made at intervals of twelve hours.

A Toepler mercury air-pump, without stop-cocks, was used in making the exhaustions. Connected with the pump was a phosphorus-pentoxide U-tube. The pentoxide that was used in the working tube was purified by subliming the commercial oxide in a stream of dry air. To prevent the pentoxide from falling into the narrow glass tube at the bottom of the working tube, a small spiral of platinum gauze was put into the narrow tube, and a loose plug of previously ignited asbestos was placed on top of the gauze. The pentoxide filled the lower compartment to within three millimeters of the constriction, and in quantity was largely in excess of the amount required to unite with the water formed. The palladium sponge was in the form of cohering masses, obtained by the reduction of pure pallad-ammonium chloride in a stream of hydrogen. It was free from ammonium chloride. The tube

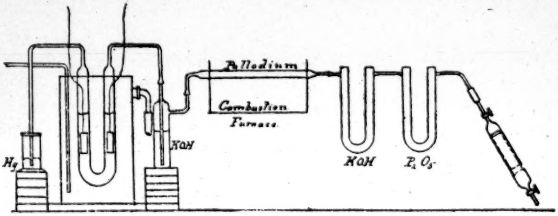


Fig. 3.

for holding the metal was open at the top, and was provided with a number of small holes near the bottom, the object of which was to facilitate the passage of the aqueous vapor from the palladium to the phosphorus pentoxide. The palladium tube when not in the working tube was kept in a desiccator over phosphorus pentoxide.

After putting the pentoxide into the working tube, exhausting and weighing it, air, dried over pentoxide, was slowly admitted. The cap was then removed and the palladium tube put into position, and the cap again instantly replaced. The tube was again exhausted and weighed. Thereupon it was charged with hydrogen. For this purpose it was connected by means of the three-way cock with an apparatus furnishing a stream of purified electrolytic hydrogen. This apparatus is shown in Fig. 3. The U-tube with electrodes for decom-

posing dilute sulphuric acid, is shown on the left. It was kept cool by means of cold water flowing in the outer cylinder. The electrolytic hydrogen passed first through a concentrated solution of caustic potash, then over palladium sponge contained in a combustion tube. The metal in the middle of the combustion tube was kept at a dull red heat; that at the ends was only slightly above the ordinary temperature. This palladium served to remove any oxygen that may have been present in the hydrogen. Other substances that might have been taken up by the palladium in the working tube would also have been removed. Thereupon the gas passed through U-tubes containing freshly fused caustic potash and resublimed phosphorus pentoxide. After the current of hydrogen had been running for about an hour and escaping at the three-way cock, it was slowly admitted to the palladium. The electrolytic oxygen escaped through the mercury shown on the extreme left. By raising or lowering the column of mercury, the pressure in the interior of the apparatus could be easily regulated.

After the palladium was saturated, the working tube was connected with the air-pump and about a liter and a half of gas was pumped out. Gas not taken up by the palladium was thus removed. After weighing, the tube was again attached to the electrolytic apparatus, which now, with reversed current, was furnishing a stream of pure dry oxygen. The oxygen was also passed over hot palladium to remove hydrogen and any other substances that might possibly be present and capable of uniting with the metal. The oxygen was dried with fused caustic potash and phosphorus pentoxide. After the oxygen had been flowing through the apparatus for about an hour and escaping at the three-way cock, the latter was cautiously opened so as to admit a very slow stream of gas. Moisture was at once deposited on the walls of the tube. If at this point a rapid stream of oxygen be admitted, the palladium at its upper surface can be seen to glow. This, however, was avoided in all the quantitative experiments recorded below. By admitting the oxygen slowly, the temperature of the working tube was not allowed to rise much above that of the surrounding air. From four to

five hours were required to oxidize the hydrogen. Finally when the tube was full of oxygen, it was allowed to stand over night. During this time most of the water combined with the pentoxide. Then the lower stop-cock was connected with the pump and the excess of oxygen withdrawn. This excess of oxygen in passing out went through the pentoxide, so that no moisture was removed from the tube in this way. The exhausted tube was weighed, and, after the palladium had been standing over the pentoxide in the vacuum for at least forty-eight hours, dry air was admitted, the palladium removed, and after again exhausting the tube was weighed. This last weighing, taken in connection with the first, gave directly the amount of water taken up by the pentoxide.

To give an idea of the details of calculation, the complete data of the second experiment are here given.

1st weighing.	2nd weighing.	3rd weighing.	4th weighing.	5th weighing.
Tube + P_2O_5 + weights against tare No. 1.	Tube + P_2O_5 + Pd + weights against tare No. 2.	Tube + P_2O_5 + Pd11 + weights against tare No. 2.	Tube + P_2O_5 + Pd + H_2O + weights against tare No. 2.	Tube + P_2O_5 + H_2O + weights against tare No. 1.
3.92084	3.67523	3.39591	1.17682	1.42185
3.92124	3.67538	3.39598	1.17714	1.42178
3.92104	3.67530	3.39594	1.17698	1.42181

Weight of hydrogen = 3.67530 — 3.39594 = 0.27936
" " oxygen = 3.39594 — 1.17698 = 2.21896

" " hydrogen + oxygen = 2.49832
" " water = 3.92104 — 1.42181 = 2.49923

Difference 0.00091

Ratio of hydrogen to oxygen = 0.27936 : 2.21896 = 1 : 7.943
" " " " water = 0.27936 : 2.49923 = 1 : 8.946

Reducing the weights to a vacuum has no appreciable effect upon the ratio. Thus reduced weight of hydrogen = 0.27936 + 0.00002 = 0.27938. Reduced weight of oxygen = 2.21896 + 0.00030 = 2.21926. Ratio H : O = 1 : 7.943. Reduced weight of water = 2.49923 + 0.00032 = 2.49955. Ratio of $H : H_2O = 1 : 8.946$.

Altogether six determinations were attempted, two of these gave results that showed that there was either leakage or imperfect drying of the gases, because the direct weight of water in one of these exceeded the sum of the weights of hydrogen and oxygen by 6 milligrams, and in the other case by 4.5 milligrams. These have accordingly been rejected. The results obtained from the others are as follows :

No.	Wt. of H.	Wt. of O.	Sum of H + O.	Wt. of H_2O found.	Difference.
1	0.27549	2.18249	2.45798	2.45975	0.00177
2	0.27936	2.21896	2.49832	2.49923	0.00091
3	0.27091	2.15077	2.42168	2.42355	0.00187
4	0.26845	2.13270	2.40115	2.40269	0.00154

Calculating the ratio of oxygen to one part of hydrogen from the second and third columns, we have :

No.	Ratio.
1	7.922
2	7.943
3	7.939
4	7.944
Mean	7.937

If the weights are reduced to a vacuum, the ratios become :

No.	Ratio.
1	7.923
2	7.943
3	7.940
4	7.945
Mean	7.937+

From the second and fifth columns we obtain the ratio of water to one part of hydrogen.

No.	Ratio.
1	8.929
2	8.946
3	8.946
4	8.950
Mean	8.943

The first ratio gives, for the atomic weight of oxygen, the number 15.874, the last one 15.886. The mean of the two is **15.880.**

BRYN MAWR COLLEGE, July 20, 1898.

ON THE METAPHOSPHIMIC ACIDS (III).[1]

By H. N. Stokes.

In the preceding papers on the metaphosphimic acids[2] it was shown that the two then known phosphonitrilic chlorides, $P_3N_3Cl_6$ and $P_4N_4Cl_8$, give, on saponification, two well-defined acids, trimetaphosphimic acid, $P_3N_3O_6H_6$ and tetrametaphosphimic acid, $P_4N_4O_8H_8$. In a later investigation[3] the existence of the higher phosphonitrilic chlorides $P_5N_5Cl_{10}$, $P_6N_6Cl_{12}$, and $P_7N_7Cl_{14}$ was shown, and it was further demonstrated that the series does not end here, but is continued through a number of members, which are incapable of separation by existing methods, and terminates with a remarkable rubber-like polymer of high molecular weight.

The work outlined in the present paper was begun with the expectation of finding that each of the new phosphonitrilic chlorides would give, on saponification, the corresponding metaphosphimic acid of the general formula $(PNO_2H_2)_n$. The result, however, has not justified this anticipation. It has been found that penta- and hexaphosphonitrilic chlorides give true penta- and hexametaphosphimic acids, $(PNO_2H_2)_5$ and $(PNO_2H_2)_6$, but that heptaphosphonitrilic chloride gives, not $(PNO_2H_2)_7$, but an acid $(PNO_2H_2)_7 + H_2O$. The metaphosphimic series, therefore, appears to be limited by the acid $(PNO_2H_2)_6$.

The metaphosphimic acids are the lactams of the imidophosphoric amides,[4] and it is therefore not surprising that there should be a certain similarity of behavior between these and certain organic oxy- and amido-acids. The γ- and δ-oxy- and amido-acids, while existing as salts in alkaline solution, pass more or less readily in the free state into the inner anhydrides, the lactones and lactams, a behavior which is not observed when the hydroxyl or amido-group is still further removed from the carboxyl. Joh. Wislicenus has shown[5]

[1] Published by permission of the Director of the United States Geological Survey.

[2] This Journal, **18**, 629, 780 (1896). [3] This Journal, **19**, 782 (1897).

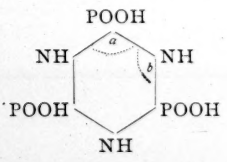
[4] The imidophosphoric acids consist of chains of alternate NH and PO groups, the first being imidodiphosphoric acid, $PO(OH)_2.NH.PO(OH)_2$. This, and diimidotriphosphoric acid are described in the paper on trimetaphosphimic acid, and triimidotetraphosphoric acid in the present paper. The amides, of which the metaphosphimic acids are the lactams, may be regarded as imidophosphoric acids having one terminal hydroxyl replaced by an amido group.

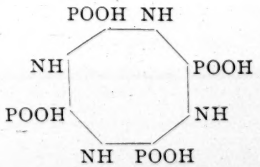
[5] Räumliche Anordnung der Atome, S. 67.

that the geometric configuration of the lactone-giving acids is such as to bring the reacting groups into close proximity, thus admitting of inner anhydride formation, while in other cases this is not possible, owing to their remoteness. Von Baeyer,[1] in his well-known "tension theory," has shown that the series of methylene-ring hydrocarbons, $(CH_2)_n$, may be expected to possess a maximum of stability in the pentamethylene ring, a ring in which there is the least "strain," because the attraction of the carbon atoms for each other acts very nearly in the direction which the valences naturally assume, a deduction which has been confirmed by recent work on the reduction of aromatic hydrocarbons, showing the tendency of these to form pentamethylene rings when reduced.[2]

The speculations of Wislicenus and Von Baeyer admit of application to the series of acids derived from the phosphonitrilic chlorides, and as far as the subject has been worked out, the analogy is a complete one. The acids in the open form are amides of imidophosphoric acids; those with from three to six phosphorus atoms have the open form in alkaline solution, from which they are thrown out by silver nitrate as salts of the general formula $(PNO_2Ag_2)_n + H_2O$, but in acid solution they spontaneously form the inner anhydrides; *i. e.*, the metaphosphimic acids, which can be precipitated as silver salts of the general formula $(PNO_2HAg)_n$. The acid with seven phosphorus atoms, on the contrary, does not form the anhydride under any conditions. Not only does the series possess an extremely marked maximum of stability in tetrametaphosphimic acid, but the higher acids, on being subjected to energetic attack, break up, yielding this body.

In my former paper, I have assumed that tri- and tetrametaphosphimic acids contain phosphorus-nitrogen rings:





[1] Ber. d. chem. Ges., 18, 2277.

[2] Zelinsky: Ber. d. chem. Ges., 30, 387, 1539.

We know nothing of the steric relations of phosphorus and but little of those of nitrogen, and have therefore no definite theoretical grounds for assuming the magnitude of the angle a formed by the lines joining a POOH group with two NH groups, nor of the angle b formed by lines connecting a NH group with two POOH groups, in the case when these are free to assume a relation of greatest stability or least tension, as in an open chain. Neither can we assert that in a six-sided ring, P_3N_3, with alternate phosphorus and nitrogen, the angles a and b must each be 120°. We are, however, justified in assuming that the *mean* of a and b is 120°. Similarly in an eight-sided ring, P_4N_4, the *mean* angle is 135°, even though a may be 180° and b 90°.

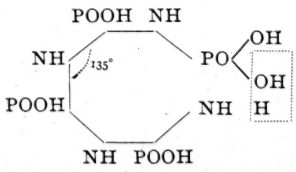
Experiment having shown that tetrametaphosphimic acid, $P_4N_4O_8H_8$, is vastly more stable than any other acid of the series, we may regard the angle $\frac{a+b}{2}$ of the octagonal nucleus P_4N_4, which is 135°, as that which most nearly coincides with the angle of least tension in the sense of Von Baeyer's theory, and as approximating to that which would be assumed in an open chain, and we may expect that the stability of each ring will be less the more the angle $\frac{a+b}{2}$ differs from 135°. In the following table the mean angle and its difference from 135° are shown :

Ring.	Number of sides.	Mean angle.	Difference from 135°.
PN	2	0°	−135°
P_2N_2	4	90°	− 45°
P_3N_3	6	120°	− 15°
P_4N_4	8	135°	0°
P_5N_5	10	144°	+ 9°
P_6N_6	12	150°	+ 15°
P_7N_7	14	154.3°	+ 19.3°
P_8N_8	16	157.5°	+ 22.5°

It is therefore to be expected that as we ascend in the series there will be a very rapid increase of stability to a maximum, followed by a gradual decrease. This coincides with what we find. $P_3N_3O_6H_6$ is vastly less stable than $P_4N_4O_8H_8$; the latter may be heated for hours with acids

without complete decomposition, while the former is destroyed under the same conditions in a few minutes.[1] $P_5N_5O_{10}H_{10}$ is much less stable than $P_4N_4O_8H_8$, but markedly more stable than $P_3N_3O_6H_6$, corresponding to the difference of only 9° from 135° in one case against 15° in the other. $P_6N_6O_{12}H_{12}$ is perceptibly less stable than $P_5N_5O_{10}H_{10}$ and finally the ring P_7N_7 of heptametaphosphimic acid is incapable of existence under the usual conditions, and as a result we get, instead of the ring acid $P_7N_7O_{14}H_{14}$, the open chain $P_7N_7O_{15}H_{16}$.

When any of the acids above tetrametaphosphimic acid is broken up, the latter is formed in considerable amount. This may be explained in two ways: either the P_4N_4 nucleus exists as such in the higher acid, or it is formed from the decomposition products. The former is highly improbable, for, considering its great stability, it should persist and be found in nearly theoretical amount, which is by no means the case. ($P_5N_5O_{10}H_{10}$ gave 12 per cent. and $P_6N_6O_{12}H_{12}$ 30 per cent. of the theoretical.) Its formation from the decomposition products is easily explained on the tension hypothesis. If a ring of POOH and NH groups be broken up by the action of a stronger acid, the molecules resulting from its decomposition will tend to assume a configuration determined by the mean angle of least tension, 135°, and this configuration in the case of the molecule of triimidotetraphosphoric amide will be either a zigzag line or the form represented by



a configuration which admits of the formation of the anhydride or lactam, which is nothing else than tetrametaphosphimic acid. A theoretical yield of this cannot be expected, for when a chain, P_5N_5, for example, is further broken up, the disruption may occur at any one of nine points, but only

[1] This JOURNAL, **18**, 653, 785.

when one of the resulting products contains P_4N_4 can tetrametaphosphimic acid be formed. A simple calculation shows that at most only 27 per cent. of that required by the equation

$$P_5N_5O_{10}H_{10} + 2H_2O = P_4N_4O_6H_8 + NH_4H_2PO_4$$

can be expected. A chain P_6N_6, however, offers more chances for the formation of fragments containing P_4N_4 and hence, as actually found, the yield of tetrametaphosphimic acid is greater, instead of less, as would be the case if the nucleus of this acid existed as such in hexametaphosphimic acid.

The first two chloronitrides, $PNCl_2$ and $P_2N_2Cl_4$, have not been obtained, and of the corresponding mono- and dimetaphosphimic acids the former is unknown and the existence of the latter questionable. Mente[1] has described salts of an acid to which he gives the formula of dimetaphosphimic acid, $P_2N_2O_4H_4$, but no proof is given that it is not some other polymer of PNO_2H_2, and the method by which he obtained it is one which is not likely to give a body of this molecular weight. The dimetaphosphimic ring would have a mean angle of 90°, which differs from that of tetrametaphosphimic acid by 45°. Such a ring should be much less stable than even that of heptametaphosphimic acid, and it is therefore quite possible that it is incapable of existence as such, and can exist only as the hydrate $P_2N_2O_5H_6$. This is perhaps the acid described by Gladstone[2] as pyrophosphodiamic acid.

The chloronitride series presents a maximum of stability in triphosphonitrilic chloride, but this is by no means as marked as that existing in the acid series. That such a maximum should occur in one case in a ring of six sides, and in the other in an eight-sided ring, and that the series should be limited in one case and unlimited in the other, involves no contradiction. Triphosphonitrilic chloride is stable only in the sense that it is formed in the largest amount and that its chlorine is most tenaciously held, while the term is applied to the acids as indicating the difficulty with which the ring is broken open. In the one case, the series consists of polymers of $-PCl_2=N-$ and in the other of $-POOH-NH-$, and

[1] Ann. Chem. (Liebig), **248**, 244.

[2] Q. J. Chem. Soc., **3**, 135, 354; Ann. Chem. (Liebig), **76**, 79; **77**, 315; J. Chem. Soc. [2], **2**, 231.

the two series cannot therefore be considered analogous in a stereochemical sense.

Only tri- and tetrametaphosphimic acids give characteristic salts. The salts of the acids with 5, 6, and 7 atoms of phosphorus are totally devoid of crystallizing power, the alkaline salts being precipitated from aqueous solution by alcohol as syrups, which can easily be converted into the solid form by dehydration with absolute alcohol, but which are still wholly amorphous. The tendency to diminished acidity of unneutralized hydroxyls, well known in the case of orthophosphoric acid, is here apparent, and to an increasing extent as we rise in the series. Trimetaphosphimic acid forms a salt with 3 atoms of sodium which has neutral reaction and is not decomposed by strong acetic acid; tetrametaphosphimic acid readily gives salts with 2 and 4 atoms of sodium. The five-atom sodium salt of pentametaphosphimic acid is strongly alkaline and shows a tendency to hydrolytic dissociation, and the same tendency is still more marked in the higher acids. Owing to this, and to their amorphous nature, it is impossible to obtain salts of definite composition from any but the first two acids, unless certain conditions are rigidly adhered to. Qualitative differences between the analogous salts of the higher acids are almost wanting, and only a quantitative study, and a knowledge of their derivation serve to distinguish them. As with other phosphorus-nitrogen acids, no ammonia is evolved on boiling with alkalies.

Amides of the Metaphosphimic Acids.

Gerhardt[1] has described, under the name "phosphamide," a body of the empirical composition PN_3OH_2, which he obtained by action of ammonia and water on phosphorus pentachloride, and to which he gave the formula $PO\begin{cases}=NH\\ NH_2\end{cases}$. This corresponds to the amide of a metaphosphimic acid, but its properties indicate that it is probably a substance of high molecular weight. I have attempted to obtain amides of the first three metaphosphimic acids by acting on the corresponding chloronitrides with gaseous or strong aqueous ammonia. The ef-

[1] Ann. chim. phys. [3], **18**, 188.

forts were but partially successful. The P : N ratio is sometimes rather higher, sometimes rather lower, than is required by the formula $(PN_2OH_2)_n$. They have none of the properties of Gerhardt's phosphamide, but are extremely soluble in water, uncrystallizable and unstable, and have weakly acid properties, forming alkali and silver salts, which, however, are of very variable composition and of ill-defined properties. Like the metaphosphimic acids, they give off no ammonia on boiling with alkali, but are easily decomposed on treatment with acids.

General Summary.

The principal results of the preceding investigations may be summed up as follows :

1. There exists a series of bodies of the general formula $(PNCl_2)_n$, beginning with Liebig's chloronitride of phosphorus, and extending indefinitely upward.

2. Each of these bodies yields, on saponification, an acid with the same number of phosphorus and nitrogen atoms.

3. The first four of these acids exist in two forms : the lactam form, $(PNO_2H_2)_n$, (metaphosphimic acids), where n is either 3, 4, 5, or 6, which is formed only in neutral or acid solution, and the open chain form $(PNO_2H_2)_n + H_2O$, formed under the influence of alkalies.

4. The acid derived from the fifth chloronitride, $P_5N_5Cl_{10}$, and possibly those from the higher members, do not form lactams, but persist in the open form under all circumstances.

5. The properties of these acids, with respect to stability, power of forming lactams, and nature of decomposition products, may be explained by stereochemical considerations, analogous to those of Von Baeyer on the methylene hydrocarbons and of Joh. Wislicenus on the lactones.

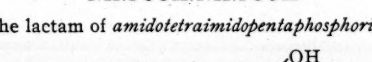
EXPERIMENTAL PART.

Saponification of the Phosphonitrilic Chlorides.—As pointed out in the preceding papers, triphosphonitrilic chloride is conveniently saponified by shaking its ethereal solution with an aqueous solution of sodium acetate, and tetraphosphonitrilic chloride in a similar manner with water, the trifling quanti-

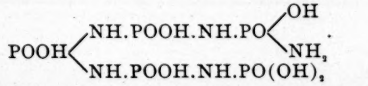
ties of secondary decomposition products being easily removed. These methods cannot be applied to the higher chlorides, for the secondary products formed by the liberated acetic or hydrochloric acid cannot be separated from the main product owing to the uncrystallizable nature of the latter. A smooth saponification without secondary products may be effected by using sodium hydroxide in sufficient amount to keep the solution always strongly alkaline.

4 parts chloride are dissolved in about 20 parts alcohol-free ether and shaken with a solution of 5 parts pure sodium hydroxide in 20 parts water. A bottle with a carefully paraffined glass stopper must be used, corks being inadmissible as they give rise to colored products which cannot be removed. The shaking is conveniently effected by a rotator, moved by a small electric motor, and about fifty hours are sufficient for complete saponification. As soon as the ether is found to be practically free from chloronitrides, the alkaline solution is drawn off and precipitated by 2 or 3 volumes of alcohol. This throws down the sodium salt as a thick syrup, which is repeatedly washed by stirring with 60 per cent. alcohol, dissolved in water, reprecipitated by alcohol and again washed in the same way until it is free from sodium chloride. It is then dehydrated by stirring, kneading, and finally pulverizing under renewed portions of absolute alcohol. After standing several hours under absolute alcohol it is filtered off and dried *in vacuo* over sulphuric acid. The yield in each case is about 90 per cent. of the theoretical, the remainder being lost in the alcoholic solution.

Pentametaphosphimic Acid,



This is the lactam of *amidotetraimidopentaphosphoric acid*,



It exists in the lactam form in the five-atom silver salt and

apparently in the solution of its acid and normal salts; in alkaline solutions, however, it has probably the open form, as the silver salt prepared from such a solution has a composition corresponding to this.

The *free acid* may be obtained, somewhat contaminated with decomposition products, by decomposing the silver salt under water by hydrogen sulphide, care being taken to keep the liquid cool. The solution has an acid, somewhat astringent, taste, and is imperfectly precipitated by alcohol in a gelatinous form, resembling precipitated alumina. This shows the reaction of the salts, but is impure, as caustic alkali causes the evolution of a little ammonia.

Sodium Salts.—As all the sodium salts are amorphous and precipitated by alcohol, in a syrupy or viscous form, it is not easy to obtain any of them pure. The salt prepared in the above manner contains about 5.4 atoms of sodium (analyses I and II) and forms a white, sandy, amorphous powder, which is not hygroscopic, but which slowly absorbs carbon dioxide. Under water it first becomes pasty and then slowly dissolves, with considerable evolution of heat. Salts with 4 or more atoms of sodium invariably contain 2 molecules of water which are retained at 100°.

The *pentasodium salt*, $P_5N_5O_{10}H_5Na_5 + 2H_2O$, may be obtained by adding to the solution of a salt containing a known excess of sodium, nearly enough nitric acid to neutralize the excess and precipitating by alcohol, or by nearly neutralizing with acetic acid, with phenolphthalein as indicator, and precipitating by alcohol. In the latter case, however, there is a slight deficiency of sodium (analyses III. and IV.) The normal salt has a strongly alkaline reaction and loses some alkali by repeated precipitation by alcohol.

For analysis the salts were dried at 100°.

	Calculated for $P_5N_5O_{10}H_5Na_5+2H_2O$.	Found. I.	II.	III.	IV.
P	28.64	28.23	28.24	29.10	29.13
N	12.96	12.90	12.86	13.29	13.22
Na	21.27	22.74	22.64	21.54	20.77

I and II were precipitated directly from alkaline solution.

I. P : N : Na = 5 : 5.02 : 5.42.

II. P : N : Na = 5 : 5.03 : 5.40.

III. and IV. were precipitated from a solution neutralized with acetic acid and phenolphthalein.

III. P : N : Na = 5 : 5.03 : 4.75.

IV. P : N : Na = 5 : 5.02 : 4.80.

The *tetrasodium salt*, $P_5N_5O_{10}H_5.Na_4H+2H_2O$, is obtained by dissolving the crude salt in water with its own weight of 80 per cent. acetic acid and precipitating twice by alcohol. It resembles the normal salt, but has neutral reaction.

It gave after drying at 100°:

	Calculated for $P_5N_5O_{10}H_5.Na_4H+2H_2O$.	Found.
P	29.85	30.02
Na	17.74	17.71

P : Na = 5 : 3.97.

Salts with still less alkali can be obtained by precipitating the crude salt by alcohol from a nitric acid solution. This precipitate is viscous rather than syrupy as with the salts with 4 and 5 atoms of sodium. Salts with 5 or more atoms of sodium can be kept indefinitely without alteration and do not evolve ammonia with alkalies, but those with less gradually decompose.

Barium Salt.—A solution of the sodium salt gives, with barium chloride, a voluminous precipitate of unknown composition, insoluble in water and acetic acid.

Magnesium Salts.—Pentametaphosphimic acid forms several salts with magnesium alone, as well as double salts with magnesium and other metals.

A solution of the sodium salt, strongly acidified with acetic acid, gives, with magnesium salts, a voluminous amorphous precipitate, nearly insoluble in water and but slightly more soluble in strong acetic acid. The composition of this, after drying at 100°, approximates to $P_5N_5O_{10}H_5.Mg_2H+5H_2O$.

	Calculated for $P_5N_5O_{10}H_5.Mg_2H+5H_2O$.	Found. I.	Found. II.
P	29.26	28.82	29.05
Mg	9.16	9.52	10.10

I. P : Mg = 5 : 2.11.

II. P : Mg = 5 : 2.22.

A considerable portion of the acid remains in solution how-

ever, even in the presence of a large excess of the precipitant, in combination with less than 2 atoms of magnesium, and can be precipitated by alcohol as a salt soluble in water. If this insoluble magnesium salt be dissolved in dilute nitric acid and ammonia added to incipient precipitation, the solution, after filtering, contains essentially the primary salt $(P_5N_5O_{10}H_9)_2Mg$; from this solution silver nitrate throws down an amorphous magnesium silver salt with a varying amount of silver. The primary salt is easily soluble in water and is remarkably stable, giving no precipitate with ammonia, sodium hydroxide or carbonate, even on boiling. The magnesium can be removed only by adding to its solution ammonia and an alkaline phosphate. On boiling in neutral or acetic acid solution, however, a precipitate of the 2-atom salt at once forms. Even the latter dissolves in boiling sodium carbonate solution.

Indications of an intermediate salt were observed, but it could not be isolated in pure condition.

Silver Salts.—The silver salts of the phosphorus-nitrogen acids are invariably free from water, and it is upon these, therefore, that the formulas of the acids themselves are based. There is no difficulty in obtaining normal silver tri- and tetrametaphosphimates of theoretical composition, and their crystalline nature affords a guarantee of their homogeneity. The same difficulty is encountered with the silver pentametaphosphimates, however, as with the sodium salts; they are amorphous flocculent precipitates, the composition of which corresponds to a definite formula only when they are formed under special conditions. In this case, as in others in this paper, the actual percentage composition expresses very little, if compared with the calculated composition of a definite salt. It is therefore better to express the results of the analysis in a molecular formula based on the atomic ratios of phosphorus, nitrogen, and silver, as actually determined; a comparison of the percentage composition found, with that calculated for salts of the lactam and open chain acids containing phosphorus and silver in the same ratio, then shows at once to which of these acids the salt is to be referred.

The composition of the precipitates depends altogether on the relative amounts of the reacting bodies and even the free

acid can be almost completely precipitated, provided a sufficient excess of silver nitrate be used. The preparations analyzed were made by precipitating a solution of 1 gram sodium salt in 50 cc. water with 55 cc. $\frac{1}{8}$-normal silver nitrate solution. To the sodium salt was added enough nitric acid to produce a salt of known composition. Under these conditions it was found that a salt with 4 atoms of sodium gives very nearly the normal salt, $P_5N_5O_{10}H_5Ag_5$ (analyses III., IV., VI.), the number of equivalents of silver in the precipitate always exceeding the number of equivalents of sodium. Up to 5 atoms of silver the precipitates are white; with more silver they become more and more yellow in proportion to the amount of silver they contain. An excess of 0.3 atom over the normal imparts a perceptible yellow tint. The salts are unaffected by light or by heating at 100°, and are decomposed by cold caustic alkalies[1] with separation of silver oxide.

In the following table the molecular formulas given are based on the ratio of phosphorus to silver actually determined and referred to the acids $P_5N_5O_{10}H_{10}$ and $P_5H_5O_{11}H_{12}$. A comparison shows that the salts are derivatives of the former, a true metaphosphimic acid. The salts were dried at 100°.

	Ratio P : N : Ag.		P.	N.	Ag.
I.	5 : 5.02 : 5.18	$P_5N_5O_{11}H_{6.82}Ag_{5.18}$	16.03	7.26	57.80
		$P_5N_5O_{10}H_{4.82}Ag_{5.18}$	16.34	7.39	58.88
		Found	16.31	7.41	58.76
II.	5 : 5.06 : 5.32	$P_5N_5O_{11}H_{6.68}Ag_{5.32}$	15.79	7.15	58.45
		$P_5N_5O_{10}H_{4.68}Ag_{5.32}$	16.09	7.28	59.55
		Found	16.04	7.35	59.37
III.	5 : 5.04 : 4.95	$P_5N_5O_{11}H_{7.05}Ag_{4.95}$	16.45	7.45	56.66
		$P_5N_5O_{10}H_{5.05}Ag_{4.95}$	16.77	7.59	57.77
		Found	16.75	7.64	57.69
IV.	5 : 4.96 : 4.96	$P_5N_5O_{11}H_{7.04}Ag_{4.96}$	16.45	7.45	56.66
		$P_5N_5O_{10}H_{5.04}Ag_{4.96}$	16.77	7.59	57.77
		Found	16.77	7.53	57.82
V.	5 : 5.04 : 5.15	$P_5N_5O_{11}H_{6.85}Ag_{5.15}$	16.09	7.28	57.65
		$P_5N_5O_{10}H_{4.85}Ag_{5.15}$	16.40	7.42	58.75
		Found	16.32	7.45	58.46
VI.	5 : 5.05 : 4.97	$P_5N_5O_{11}H_{7.03}Ag_{4.97}$	16.42	7.43	56.78
		$P_5N_5O_{10}H_{5.03}Ag_{4.97}$	16.74	7.57	57.89
		Found	16.62	7.59	57.51

[1] $P_5N_5O_4H_5Ag_5$ is scarcely affected by boiling with strong caustic potash and $P_4N_4O_6H_4Ag_4$ is scarcely affected in the cold, but is at once decomposed on boiling.

Tri- and tetrametaphosphimic acids, when precipitated from ammoniacal solution by excess of silver nitrate, gave amorphous yellow salts of the composition $P_3N_3O_7H_2Ag_4$ and $P_4N_4O_9H_2Ag_8$ respectively.[1] These are salts of the open chain acids. A similar salt is obtained by precipitating an ammoniacal solution of pentametaphosphimic acid by silver nitrate, but in accordance with its less acid properties the quantity of silver does not reach 10 atoms, being in the specimen analyzed only 8.76 atoms, but the figures correspond closely to a derivative of *amidotetrimidopentaphosphoric acid*, $P_5N_5O_{11}H_{12}$, rather than pentametaphosphimic acid. Dried at 100° it gave :

Ratio P : Ag.			
5 : 8.76	$P_5N_5O_{11}H_{3.24}Ag_{8.76}$	11.49	70.04
	$P_5N_5O_{10}H_{1.24}Ag_{8.76}$	11.64	70.98
	Found	11.48	70.03

It appears, therefore, that in alkaline solution the metaphosphimic acids become open-chain acids, just as lactones and lactams give γ- and δ-oxy- and amido-acids. On drying at 100°, the yellow silver salts become gray without loss of weight, probably owing to separation of silver oxide. This is perhaps due to a tendency to revert to the lactam form, with separation of silver oxide, rather than water.

Decomposition of Pentametaphosphimic Acid.—Pentametaphosphimic acid is markedly more stable in acid solution than trimetaphosphimic acid. In my paper on the latter I described in detail its decomposition products when acted on by nitric acid.[2] Under identical conditions the rate of decomposition of pentametaphosphimic acid was found to be very much slower. On account of this greater stability the action of hot acetic acid gives more satisfactory results. No attempt was made to isolate all the products, as these are numerous and the analytical difficulties considerable. The following were identified :

[1] This JOURNAL, 18, 651, 788. The formula $P_4N_4O_9Ag_8$ was there ascribed to the persilver salt of tetrametaphosphimic acid; a recalculation of the analyses in the above manner, however, shows that they correspond much more closely to the open form $P_4N_4O_9H_2Ag_8$, with a slight deficiency of silver.

[2] This JOURNAL, 18, 653.

Tetrametaphosphimic acid, $P_4N_4O_6H_8$.
Triimidotetraphosphoric acid, $P_4N_3O_{10}H_9$.
Diimidotriphosphoric acid, $P_3N_3O_8H_7$.
Orthophosphoric acid, H_3PO_4.

5 parts sodium pentametaphosphimate are dissolved in 15 parts water, 5 parts strong acetic acid added, and the solution heated in the water-bath. The separation of a crystalline precipitate of acid sodium tetrametaphosphimate begins in about fifteen minutes and continues for perhaps eight hours, at the end of which time the solution gives no precipitate with magnesium chloride, indicating the absence of pentametaphosphimate. The sodium tetrametaphosphimate, being insoluble in a solution of sodium salts, is completely precipitated. It is filtered off and washed a little with a saturated sodium acetate solution. The filtrate is concentrated to about one-half with addition of about 5 parts solid sodium acetate, whereby sodium triimidotetraphosphate separates, in the form of flat prisms or plates, which are washed with a little saturated sodium acetate solution and purified by dissolving in water and precipitating by alcohol, or by adding solid sodium acetate to their hot solution. On further concentrating the filtrate, large plates are often obtained, which give, with silver nitrate and nitric acid, a crystalline precipitate of the characteristic silver diimidotriphosphate, $P_3N_3O_8H_4Ag_3$.[1] No satisfactory and certain method can be given for the separation of these two acids.

The sodium tetrametaphosphimate thus obtained usually has the form of spindles, but, when well developed, consists of brilliant double pyramids. It had not been observed at the time of writing the paper on tetrametaphosphimic acid. It is obviously an acid sodium salt, as it is formed only in the presence of acetic acid or a limited amount of a stronger acid. It was also obtained directly from the original sample of the acid, but was not analyzed, as it is difficult to obtain a sufficient quantity uncontaminated by the free acid. It is moderately soluble in water, but almost insoluble in solutions of sodium salts and is highly characteristic of this acid. The crude salt was dissolved in ammonia, with the addition of

[1] This JOURNAL, 18, 657.

some ammonium nitrate, and precipitated by nitric acid as $P_4N_4O_8H_4(NH_4)_2$.[1] The precipitation is almost quantitative. This pure salt was dissolved in ammonia, largely diluted, and, after acidifying with nitric acid, precipitated by an excess of silver nitrate in the form of the characteristic $P_4N_4O_8H_4Ag_4$. This gave:

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found.
P	16.68	16.88
N	7.55	7.56
Ag	58.03	57.51

The free acid was obtained by decomposing the silver salt with hydrochloric acid in the characteristic form of difficultly soluble needles. It gave:

	Calculated for $P_4N_4O_8H_8 + 2H_2O$.	Found.
P	35.22	35.08
N	15.94	15.75

A comparison of the acid potassium, sodium, and ammonium salts and neutral ammonium salt with those prepared from a sample of tetrametaphosphimic acid from tetraphosphonitrilic chloride showed them to be identical in form. The yield of tetrametaphosphimic acid appears to be nearly independent of proportions and concentration, and was about 12 per cent. of that required by the equation

$$P_5N_5O_{10}H_{10} + 2H_2O = P_4N_4O_8H_8 + NH_4H_2PO_4.$$

Triimidotetraphosphoric Acid, $PO(OH)_2.NH.POOH.NH.POOH.NH.PO(OH)_2$.—The sodium salt of this, the third member of the imidophosphoric acid series obtained,[2] crystallizes well in small rhombic or six-sided plates. The several specimens obtained were not analyzed, but converted into the silver salt. By analogy with $P_3N_3O_8H_7$, there can be little doubt that it is the acid salt, $P_4N_3O_{10}H_4Na_4$. It is easily soluble in water, but almost insoluble in saturated sodium acetate solution or dilute alcohol. It gives a precipitate with magnesium nitrate only on adding ammonia and ammonium chloride, when a voluminous precipitate is obtained, which, on standing, slowly changes to minute crystalline spherules.

[1] This JOURNAL, **18**, 786.

[2] *Ibid*, **18**, 635, 653.

Silver Triimidotetraphosphate, $P_4N_3O_{10}H_5Ag_4$, is obtained as a voluminous amorphous white precipitate by adding silver nitrate to a solution of the sodium salt faintly acidified with nitric acid. On long standing under its mother-liquor it becomes crystalline and this change occurs in a few moments on washing the precipitate, shrinking to a heavy, sandy, crystalline powder, a very characteristic behavior. The same change can be observed under the microscope in the partially washed salt, the amorphous portion changing to minute particles showing active Brownian movement, which aggregate to prisms which are long and pointed and often tufted at the ends, and which cannot be distinguished in appearance from silver tetrametaphosphimate. From a decidedly acid solution the salt is deposited slowly and without the intermediate amorphous form.

The salt gave after drying at 100°:

	Calculated for $P_4N_3O_{10}H_5Ag_4$.	Found. I.	II.
P	16.26	16.43	16.48
N	5.52	5.62	5.55
Ag	56.58	56.61	57.18

I. P : N : Ag = 4 : 3.03 : 3.96.

II. P : N : Ag = 4 : 2.98 : 3.99.

Triimidotetraphosphoric acid could not be obtained from tetrametaphosphimic acid, being much less stable than the latter. It is therefore probably derived from the breaking-down of the chain of phosphorus and nitrogen atoms formed by the hydrolysis of the pentametaphosphimic ring.

Hexametaphosphimic Acid,

$$NH\begin{cases}POOH.NH.POOH.NH.POOH\\POOH.NH.POOH.NH.POOH\end{cases}NH.$$

—This is the lactam of amido-pentimidohexaphosphoric acid,

$$NH\begin{cases}POOH.NH.POOH.NH.PO\begin{cases}OH\\NH_2\end{cases}\\POOH.NH.POOH.NH.PO(OH)_2\end{cases}.$$

It is obtained as sodium salt by saponifying hexaphosphonitrilic chloride in ethereal solution by sodium hydroxide in the

manner above described. In neutral or acid solution it has the lactam form, as shown by the composition of the silver salt, but in alkaline solution it has presumably the open form. The *free acid* obtained in solution by decomposing the silver salt under water by hydrogen sulphide has an astringent rather than acid taste, and cannot be obtained pure in the solid form, as it is not precipitated by alcohol, and the solution, on evaporating, undergoes much decomposition, leaving a gummy residue.

Sodium Hexametaphosphimate, $P_6N_6O_{12}H_6Na_6 + 2H_2O$.—The properties of this salt are essentially the same as those of the corresponding pentametaphosphimate. When containing an excess of alkali it is stable, but with a deficiency, it decomposes more or less rapidly. A salt of approximately normal composition can be obtained by adding to the solution of a preparation with more than 6 atoms of sodium enough nitric acid to neutralize the excess and precipitating by alcohol (analyses III. and IV.) .In the following table the results are expressed in formulas based on the determined ratio P : Na. The samples were dried at 100°.

	Ratio P : N : Na.		P.	N.	Na.
I.	6:6.02:6.35	$P_6N_6O_{12}H_{5.65}Na_{6.35}+2H_2O$	28.62	12.95	22.50
		Found	28.55	12.96	22.45
II.	6:...:6.46	$P_6N_6O_{12}H_{5.54}Na_{6.46}+2H_2O$	28.51	....	22.80
		Found	28.31	....	22.63
III.	6:6.04:5.93	$P_6N_6O_{12}H_{6.07}Na_{5.93}+2H_2O$	29.02	13.14	21.31
		Found	29.13	13.27	21.38
IV.	6:6.05:5.94	$P_6N_6O_{12}H_{6.06}Na_{5.94}+2H_2O$	29.02	13.14	21.31
		Found	29.16	13.29	21.43
V.	6:...:4.60	$P_6N_6O_{12}H_{7.40}Na_{4.60}+2H_2O$	31.05	....	17.70
		Found	30.89	....	17.60

I. and II. precipitated from solution containing excess of alkali.

III. and IV. from solution in which excess over 5 Na had been neutralized.

V. from solution in large excess of acetic acid.

Magnesium Salt.—A solution of the sodium salt, precipitated by magnesium nitrate in the presence of acetic acid, under exactly the same conditions as were observed in preparing

the corresponding pentametaphosphimate, gave a salt which closely resembles the latter, but which does not approximate to any definite formula (found P : Mg = 6 : 2.43). The precipitation is by no means complete, much remaining in solution as a salt which can be precipitated by alcohol, which is not decomposed by boiling with alkalies, and which, in general, resembles the primary salt of pentametaphosphimic acid.

Silver Hexametaphosphimate, $P_6N_6O_{12}H_6Ag_6$.—The silver salt, prepared from the sodium salt, varies in composition with the relative amounts of the reacting bodies and with the amount of sodium. It was obtained of normal composition by dissolving 1 gram sodium salt in 50 cc. water, adding enough nitric acid to produce a salt with 5.75 atoms of sodium, and precipitating by 50 cc. $\frac{1}{5}$-normal silver nitrate (analyses III. and IV.). It resembles the corresponding pentametaphosphimate, but is somewhat more gelatinous. Any excess of silver over 6 atoms tends to give it a yellow color. It is decomposed in the cold by caustic potash with separation of silver oxide. The analyses given in the following table of preparations dried at 100°, show that it is derived from the true hexametaphosphimic acid, $P_6N_6O_{12}H_{12}$.

	Ratio P : N : Ag.		P.	N.	Ag.
I.	6 : 6.08 : 5.65	$P_6N_6O_{12}H_{6.35}Ag_{5.65}$	16.97	7.68	55.60
		$P_6N_6O_{12}H_{6.35}Ag_{5.65}$	17.26	7.81	56.53
		Found	17.23	7.89	56.48
II.	6 : ... : 6.21	$P_6N_6O_{12}H_{5.79}Ag_{6.21}$	16.09	...	57.97
		$P_6N_6O_{12}H_{5.79}Ag_{6.21}$	16.35	...	58.89
		Found	16.29	...	58.64
III.	6 : 5.99 : 5.98	$P_6N_6O_{12}H_{6.02}Ag_{5.98}$	16.44	7.44	57.02
		$P_6N_6O_{12}H_{6.02}Ag_{5.98}$	16.71	7.56	57.95
		Found	16.70	7.54	57.90
IV.	6 : 6.04 : 6.02	$P_6N_6O_{12}H_{5.98}Ag_{6.02}$	16.38	7.41	57.18
		$P_6N_6O_{12}H_{5.98}Ag_{6.02}$	16.65	7.54	58.02
		Found	16.57	7.54	57.80

A yellow salt is obtained by precipitating the ammoniacal solution by silver nitrate.

Decomposition of Hexametaphosphimic Acid.—The sodium salt heated with acetic acid gives tetrametaphosphimic acid, which was isolated in the manner described above. The yield is 30 per cent. of that required by

$$P_6N_6O_{12}H_{12} + 4H_2O = P_4N_4O_8H_8 + 2NH_4H_2PO_4.$$

After purifying, it was converted into the silver salt which gave:

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found.
P	16.68	16.63
N	7.55	7.50
Ag	58.03	57.58

P : N : Ag = 4 : 3.99 : 3.98.

Comparison of the crystals of free acid and of the acid and neutral ammonium salts, acid potassium salt, neutral sodium salt, and silver salt with similar preparations made from tetraphosphonitrilic chloride showed that they were identical.

The decomposition products were not further studied.

Amidoheximidoheptaphosphoric Acid, $P_7N_7O_{18}H_{16}$.

The saponification of heptaphosphonitrilic chloride is effected in the usual manner with sodium hydroxide. As before pointed out, this acid does not give the lactam, heptametaphosphimic acid, even in acid solution, the silver salt having the composition of a salt of the open-chain acid.

Sodium Salt.—The properties of this salt are similar to those of sodium penta- and hexa-metaphosphimate. Dried *in vacuo* and at 100° it gave:

P : Na = 7 : 7.43.

	Calculated for $P_7N_7O_{18}H_{8.57}Na_{7.43} + 2H_2O$.	Found.
P	28.16	28.31
Na	22.19	22.31

Silver Salt, $P_7N_7O_{18}H_9Ag_7$.—To obtain a salt of normal composition 1 gram sodium salt is dissolved in 50 cc. water, enough nitric acid is added to form a salt with 6.85 atoms of sodium and precipitated by 50 cc. $\frac{1}{8}$-normal silver nitrate. More sodium or silver nitrate gives a salt richer in silver. The salt forms a white semigelatinous precipitate, which dries *in vacuo* to translucent brittle lumps which were pulverized, dried again *in vacuo* and then carefully to constant weight at 100°.

	Ratio P : N : Ag.		P.	N.	Ag.
I.	7 : ... : 6.93	$P_7N_7O_{15}H_{9.07}Ag_{6.93}$	16.55	...	56.99
		$P_7N_7O_{14}H_{7.07}Ag_{6.93}$	16.77	...	57.77
		Found	16.44	...	56.61
II.	7 : ... : 7.21	$P_7N_7O_{15}H_{8.79}Ag_{7.21}$	16.17	...	57.97
		$P_7N_7O_{14}H_{6.79}Ag_{7.21}$	16.40	...	58.76
		Found	16.21	...	58.09
III.	7 : ... : 7.08	$P_7N_7O_{15}H_{8.92}Ag_{7.08}$	16.35	...	57.51
		$P_7N_7O_{14}H_{6.92}Ag_{7.08}$	16.57	...	58.30
		Found	16.27	...	57.27
IV.	7 : 7.04 : 7.03	$P_7N_7O_{15}H_{8.97}Ag_{7.03}$	16.41	7.43	57.35
		$P_7N_7O_{14}H_{6.97}Ag_{7.03}$	16.64	7.53	58.16
		Found	16.35	7.44	57.14

These figures show, beyond question, that the acid has the open form $P_7N_7O_{15}H_{16}$.

The decomposition of the sodium salt by acetic acid gives rise to a considerable amount of tetrametaphosphimic acid, characterized by its crystalline form and that of its salts.

Higher Acids.—Of the higher acids of the series but little can be said. The oil remaining over from preparation of chloronitrides and which has a mean molecular weight nearly corresponding to $P_{11}N_{11}Cl_{22}$,[1] on saponification gives a mixture of sodium salts which are precipitated by alcohol in a decidedly viscous form, and which are decomposed by acids, give tetrametaphosphimic, diimidotriphosphoric, and triimidotetraphosphoric acids. They were not further investigated.

Amides of Metaphosphimic Acids.

Amides of $P_3N_3O_4H_4$.—Strong ammonia gas acts slowly on a solution of $P_3N_3Cl_6$ in absolute ether, the product being at first ammonium chloride and the chloramide,[2] $P_3N_3\begin{matrix}Cl_4\\(NH_2)_2\end{matrix}$. This remains in solution and is gradually attacked further, but is the only product of the reaction which is soluble in ether; by further action of ammonia the chlorine is further substituted, but never completely, and the reaction product is thrown down, mixed with ammonium chloride. On washing this with alcohol, dissolving in water, and treating with

[1] This JOURNAL, 19, 793. [2] *Ibid*, 17, 286.

enough silver nitrate to precipitate the chlorine, a solution is obtained which, by fractional precipitation with silver nitrate, gave the silver salt of an amide with the ratio P : N : Ag = 3 : 6.27 : 2.01. An ethereal solution of $P_3N_3\begin{cases}Cl_4\\(NH_2)_2\end{cases}$, shaken with sodium hydroxide, gives the sodium salt of the diamide of trimetaphosphimic acid, from which the chlorine may be removed by neutralizing with nitric acid and adding the calculated amount of silver nitrate. From the filtrate an amorphous silver salt may be precipitated which gave the ratio P : N : Ag = 3 : 4.88 : 3.51. If $P_3N_3Cl_6$, $P_4N_4Cl_8$, or $P_5N_5Cl_{10}$, in ethereal solution is shaken with ammonia of sp. gr. 90, a strong reaction occurs at first, whereby a portion of the chlorine is replaced. On shaking two or three hours, the remainder is removed. The excess of ammonia was removed from the aqueous solution by blowing air through and the chlorine precipitated by the theoretical amount of silver nitrate. The ammonium salts of the amides thus obtained were thrown down by alcohol as syrups which cannot be hardened under absolute alcohol. If these solutions are precipitated by silver nitrate, after adding a little ammonia, amorphous white precipitates of the amido silver salts are obtained, which do not show a constant composition. Analysis gave the following atomic ratios:

Amide from P_3N_3Cl—P : N : Ag = $\begin{cases}3 : 5.80 : 2.20\\3 : 5.96 : 3.36\\3 : 6.54 : 3.08\end{cases}$

Amide from $P_4N_4Cl_8$—P : N : Ag = $\begin{cases}4 : 8.80 : 4.82\\4 : 9.28 : 4.03\end{cases}$

Amide from $P_5N_5Cl_{10}$— P : N : Ag = 5 : 10.16 : 2.64

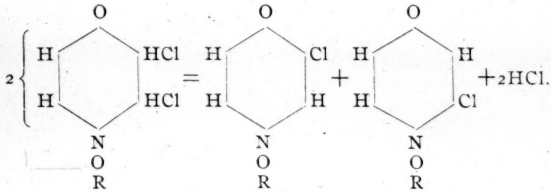
From these figures it appears that the amides are of very varying composition. As they are amorphous and very unstable, it is unlikely that any definite bodies can be obtained in this way. The silver salts are turned yellow by potassium hydroxide, a portion of the amide going into solution and a salt with a higher proportion of silver being formed.

U. S. Geological Survey.
Washington, D. C., August, 1898.

THE ETHERS OF TOLUQUINONEOXIME AND THEIR BEARING ON THE SPACE ISOMERISM OF NITROGEN.

By John L. Bridge and Wm. Conger Morgan.

In an article on the ethers of quinoneoxime (isonitrosophenol) published by one of us,[1] it was stated, that when boiled with alcohol, the benzoyl ether of quinoneoxime dichloride gave two monochlor substitution-products. Naturally it was supposed that the chlorine atom occupied, in the one, an ortho position and in the other, a meta position to the radical NOR, the reaction being :

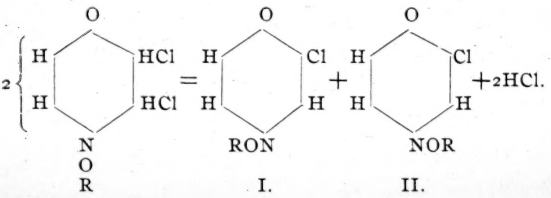


It was also found that these same isomers were formed when monochlorquinone was treated with hydroxylamine hydrochloride, and the sodium salt of the chlorquinoneoxime thus formed, treated with benzoyl chloride.

The preceding explanation regarding the splitting off of hydrochloric acid from the dichloride is not in accord with results of work done by Kehrman,[2] published in his article on the influence of radicals in the action of hydroxylamine on quinones, in which he generalizes the results of his observations in the statement that the presence of a radical attached to the ring so much lessens the replaceability of the quinone oxygen atom neighboring to the radical that the principal part, if not the whole of the resulting product, is a meta-substituted quinoneoxime. The work of his former article has

[1] Ann. Chem. (Liebig), **277**, 79.
[2] Ber. d. chem. Ges., **21**, 3315; J. prakt. Chem. [2], **40**, 258.

been repeated by Kehrman,[1] who finds the same isomeric benzoyl ethers of monochlorquinoneoxime; but, believing that observations of their behavior indicate the substantiation of his rule, he states that both these ethers have the chlorine atom in the meta position to the oximido group, and attributes their difference to space isomerism of nitrogen, writing the reaction thus:



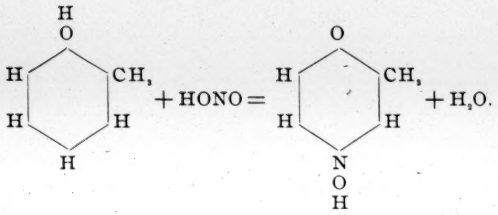
I. II.

Kehrman designates the compound represented by symbol I. as "chlorquinonemetaantioxime ether" and II. as "chlorquinonemetasynoxime ether." The question as to whether the chlorine atom occupies the same position in both compounds could be definitely settled if ortho- and metachlorphenols could be changed to the corresponding chlorquinoneoximes or so-called isonitrosophenols. This transformation has, however, unfortunately not yet been accomplished, and repeated efforts to obtain the corresponding bromquinoneoximes have resulted in failure, orthobromphenol not being attacked by nitrous acid or amyl nitrite.

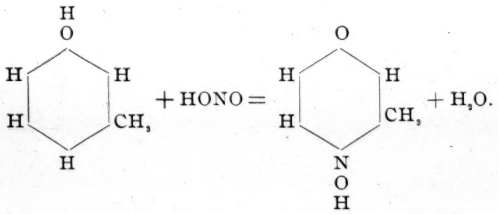
The toluquinoneoximes obtained by the action of nitrous acid on ortho- and metacresol, we have taken up for study as being the most closely analogous compounds in which the position of the side groups is definitely known, believing that by an examination of these bodies, light may be thrown upon the nature of the others.

When orthocresol is acted upon by nitrous acid, a toluquinonemetaoxime is formed according to the following reaction:

[1] Ann. Chem. (Liebig), **279**, 27.



The metacresol forms similarly a corresponding orthooxime:



The benzoyl ethers of the toluquinoneoximes prove to be exceedingly well fitted to characterize these bodies since they are formed from the oximes in quantitative proportions, are easily crystallized, and readily distinguished from each other.

The benzoyl ether of toluquinoneorthooxime produced from metacresol, crystallizes in light brownish-yellow crystals, melting at 177° C. and appearing under the microscope as long rectangular blades, suggesting the orthorhombic system. The benzoyl ether of toluquinonemetaoxime produced from orthocresol is obtained in the form of yellow crystals which begin to soften at about 150° and do not melt entirely until at about 190°. Subjected to fractional crystallization, a portion of the metaoxime so readily obtained consisting of branching needle-like crystals, melting at 193° C. These, as well as lower-melting fractions, can be readily distinguished from the orthooxime by their less regular appearance under the lens, as well as by their crystal habit, tending to produce curved forms.

The marked difference in the form and habit of the crystals

of the benzoyl ethers of the ortho- and metatoluquinone oximes makes it possible to study carefully the product of the action of toluquinone on hydroxylamine. Goldschmidt and Schmidt[1] have shown that the principal product of this reaction is toluquinonemetaoxime. This they demonstrated by oxidizing to a dinitro compound; but as some of the theoretically possible nitro-derivatives of the cresols are not known, this method can scarcely be considered to prove conclusively the absence of toluquinoneorthooxime. We have, therefore, studied further the product of the action of hydroxylamine on toluquinone by the aid of the benzoyl ethers. When the sodium salt of the oxime thus formed was treated in alcoholic solution with benzoyl chloride, and the benzoyl ether obtained was subjected to fractional crystallization, not a trace of the orthooxime ether, crystallizing in blades and melting at 177° C., was found. This proves that when toluquinone is treated with hydroxylamine the whole of the resulting product is toluquinonemetaoxime. The inference is plain that Kehrman's rule concerning the influence of side-chains, attached to the ring in quinones, upon the entering oximido radical is quantitatively true in this case; and similar indications furnished by the corresponding methyl ethers, as will appear later, strengthen this conclusion.

As has been previously shown, the benzoyl ether of the metaoxime does not consist of a single compound, but is a mixture. The body melting at 193° C. is readily separated in considerable quantities, while the remainder consists of a very intimate mixture of this body with one of much lower melting-point, separated, if it can be separated at all, only with the greatest difficulty. By concentration of the mother-liquor from which the high-melting fractions have been obtained, and carefully crystallizing, fractions may be separated melting almost completely at temperatures, varying with the fraction, between 130° and 150° C. Repeated crystallizations separated each fraction into portions melting, on the one hand, always considerably higher, and, on the other hand, often somewhat lower, and ordinarily no definite body of low melting-point could be isolated. Twice, however, a nearly

[1] Ber. d. chem. Ges., 17, 2063.

complete separation seemed to have been obtained. Thus, from fractions melting between 140° and 150°, a few short, thick prisms melting once at 142° and again at 144° C. separated, leaving the compound which melts at 193°. Of these crystals there was not enough for a combustion, but an analysis of a fraction melting almost completely at 137° gave figures which show without doubt that this portion had the same percentage composition as the body melting at 193°. If we are to regard the product as it is first obtained as a mixture of two ethers, and consider that 142°–144° is the melting-point of the lower body, we can account for the melting of fractions below 142° on the ground that mixtures may have a lower melting-point than either of the component substances. These results were obtained repeatedly from three separate portions of Kahlbaum's C. P. orthocresol, purchased at different times, as well as from toluquinone melting at 67° C. and wholly volatile when exposed to the air.

When the silver salt of toluquinonemetaoxime acts upon methyl iodide, the product is, likewise, not a single ether but a mixture of ethers, softening at 55° and not melting completely below 70°. From it a body melting at 73°–74° C. can easily be separated, but no other compound of definite melting-point or different crystal form could be obtained.

The acetyl compound of toluquinonemetaoxime presents phenomena similar to those of the benzoyl ethers, but in rather more marked degree. The product, as first obtained by the action of acetyl chloride on the silver salt of the oxime, or by acetic anhydride on the oxime itself, begins to soften at 90° and melts completely at 110°. Upon the first recrystallization a distinction in crystal form appears, and a second crystallization of the separated portions gave short, thick prisms melting at 112°–113° C., and some smaller, spherically grouped crystals, melting at 85°–87° C. The extreme difficulty of preparing the acetyl compound prevented further investigation.

In like manner, the benzoyl ether of monobromtoluquinonemetaoxime seems to be a mixture of isomeric bodies. Thus, it was found possible to add two atoms of bromine to the ethers

of toluquinoneoxime forming colorless dibromides corresponding to the dibrom addition-products of quinoneoxime, and these dibromides, when boiled with dilute alcohol, split off hydrobromic acid with the formation of colored monobrom substitution-products. The benzoyl ether of monobromtoluquinonemetaoxime thus formed shows a variation in melting-point similar to that of the ethers previously discussed.

The foregoing facts speak in favor of Kehrmann's theory of space isomerism in the oximes so far as the metaoximes are concerned. On the other hand, there is no evidence to show the presence of isomers in the ethers of toluquinoneorthooxime: the methyl, acetyl, and benzoyl ethers all act as simple substances, each product melting completely at a definite temperature. It is difficult to understand why isomerism should be so much more evident in the ethers of toluquinonemetaoxime than in the ethers of the orthooximes, unless, possibly, the closer proximity of the side-chain to the oximido-group prevents the formation of a space isomer. There is, however, a remote possibility that isomeric bodies may exist, so similar in properties that they cannot be detected by the ordinary methods.

Experimental Part.

Preparation of the Oximes and their Salts.

The toluquinone-, ortho-, and metaoximes used in the experiments to be described were made in the following manner: To a solution of 10 grams of cresol and 8 grams of potassium nitrite in 900 cc. of water, a solution of 6 grams of concentrated sulphuric acid in 100 cc. of water was added in small portions during the course of half an hour, care being taken that both original solutions should be between 5° and 10° C., and that this temperature be maintained during the mixing. Nearly all of the oxime separates out on standing in ice-water for one to two hours, and after filtering and washing with 200-300 cc. of ice-water, the amount of oxime obtained by extracting the filtered solution with ether is so small that it may be disregarded. The substances were purified by dissolving in a saturated solution of sodium carbonate and filtering into

dilute sulphuric acid, cooled with ice. At this stage it is generally ready for use, but if further purification is desired, it may be accomplished by dissolving the oxime in ether and shaking with animal charcoal. Upon filtering and evaporating, the oxime crystallizes in long, slightly colored needles. The yield is large in both cases, that of the orthooxime being nearly theoretical. As given by Beilstein, toluquinone-*m*-oxime melts at 134° C.; toluquinone-*o*-oxime melts at 155° C.; Beilstein gives 145°–150°.

The silver salt of the metaoxime was made in the following manner: 5 grams of toluquinone-*m*-oxime was dissolved in a solution of sodium hydroxide, a little less than the quantity calculated to form the sodium salt, and this solution was filtered into 500 cc. of water containing $1\frac{1}{3}$ times the calculated amount of silver nitrate. The precipitate comes down in a flocky, gelatinous condition, but goes over into a granular form on heating to 50° C. in a water-bath. When dissolved in the least possible amount of warm dilute ammonia, and the solution precipitated with hydrochloric acid,

0.1006 gram of the substance, dried over H_2SO_4, gave 0.0590 gram AgCl.

	Calculated for $C_7H_4NO_2Ag$.	Found.
Ag	44.23	44.14

The salt is light reddish-brown when first formed, but turns darker on standing or heating. It decomposes when heated to 100° and, when thoroughly dry, is spontaneously inflammable at a temperature above 60°. It is a rather unstable body and cannot be kept long when at all impure.

The silver salt of toluquinone-*o*-oxime was made in the manner described for the preparation of the silver salt of the meta form. The salt falls in the cold as reddish-brown crystals, tending to darken when exposed to light or heat.

Dried over H_2SO_4, 0.2560 gram gave 0.1498 gram AgCl.

	Calculated for $C_7H_4NO_2Ag$.	Found.
Ag	44.23	44.06

Although very similar in all its properties to the silver salt of toluquinone-*m*-oxime, this salt is, like all the ethers of the

ortho form, much more stable than its corresponding meta isomer.

Toluquinone-m-oxime Methyl Ether.

From o-Cresol.—Of the silver salt of toluquinone-*m*-oxime, 2 or 3 grams were suspended in 10–15 cc. of ligroïn and twice the calculated quantity of methyl iodide added. After standing for an hour with frequent shaking, the liquid was filtered off and the residue extracted with a little hot ligroïn. The united ligroïn solutions were allowed to evaporate spontaneously, and the methyl ether came out in large, dark-yellow, hexagonal prisms. A little more may be obtained by allowing the residue to stand for a week with methyl iodide. The yield in any case is small, the best results apparently being obtained by using not more than 2 or 3 grams of the silver salt at one time. After purifying with animal charcoal and recrystallizing from ligroïn, the product obtained softens at 55° yet does not melt completely below 70°. Portions melting at 73°–74° C. were separated by fractional crystallization, and, on analysis,

0.1101 gram of this body, dried over H_2SO_4, gave 0.2582 gram CO_2 and 0.0599 gram H_2O.

0.0881 gram of the substance gave 7.1 cc. N at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	63.96
H	6.00	6.05
N	9.29	9.59

Although fractions were often obtained melting from 55°–60°, no other compound of very definite melting-point could be separated. The methyl ether is very soluble in all organic reagents; in hot ligroïn it is much more soluble than in cold, from which it crystallizes in small bright-yellow prisms.

From Toluquinone.—To a solution of 2 grams of toluquinone in 800 cc. of water, the calculated amount of methoxylamine hydrochloride was added. Yellow crystals began to precipitate in the course of two hours, and at the end of twelve hours the reaction was completed. The liquid was filtered off and

extracted with ether, which, upon evaporation, left behind a yellow crystalline mass. The two portions were united and recrystallized from ligroïn. The yield was very good, being 75 per cent. of the theory. Even after boiling in ligroïn with animal charcoal and recrystallizing several times, the substance acts like a mixture, softening at 58° and melting at 70°. A portion, less soluble than any other, was easily separated, which melted at 73°–74° C. and was identical in all respects with the methyl ether obtained from the silver salt of toluquinone-*m*-oxime made from *o*-cresol.

0.1263 gram, dried over H_2SO_4, gave 0.2962 gram CO_2 and 0.0672 gram H_2O.

0.2952 gram gave 25 cc. N at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	63.96
H	6.00	5.91
N	9.29	10.00

Toluquinonemetaoxime Acetyl Ether.

This ether can be made in two ways: By adding the calculated amount of acetyl chloride, drop by drop, to 2–3 grams of the silver salt suspended in 15–20 cc. of ligroïn or absolute ether, kept cool by ice-water, evaporating at once, and extracting the residue with hot ligroïn; or by heating 1 molecule of the oxime on the water-bath for an hour with 1.5 molecules of acetic anhydride, adding cold water, filtering off the tarry mass which separates, and extracting it with hot ligroïn. The yield by either method is extremely poor, and sometimes after purifying by boiling with animal charcoal, the total product consisted of a few small crystals. By fractional crystallization two portions were separated, the less soluble composed of thick irregular prisms melting at 112°–113° C., and a much smaller fraction of minute, spherically grouped crystals, melting at 85°–87° C. In analyzing the original product unfractioned:

0.0053 gram, dried over H_2SO_4, gave 0.2090 gram CO_2 and 0.0444 gram H_2O.

0.0848 gram gave 5.8 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_9H_9NO_2$.	Found.
C	60.30	59.91
H	5.06	5.18
N	7.84	8.01

The acetyl ether is very soluble in alcohol and ether, much less in ligroïn, and very little soluble in water.

Toluquinone-m-oxime Benzoyl Ether.

From o-Cresol.—This ether can be made from the silver salt suspended in absolute ether, or, better, from the sodium salt in alcohol solution. Slightly less than the amount of sodium calculated to form a sodium oxime is dissolved in 100 cc. of alcohol, 2–5 grams of the oxime added, and into the filtered solution slightly more than the theoretical quantity of benzoyl chloride is dropped slowly, the solution being kept cool. The benzoyl ether begins to separate immediately, and after a few moments the alcohol can be filtered off and rejected, as it contains little of the substance. After boiling in alcohol with animal charcoal, when the solution is submitted to fractional crystallization, three-fourths of the crude product can be readily separated in the form of bright-yellow needles melting at 193° C. Upon concentrating the mother-liquor to a small volume and cooling, nearly the theoretical quantity of the benzoyl ether can be recovered. Nothing further was ever obtained save a few flakes of benzoic acid formed by the saponifying action of hydrochloric acid, produced by the slight excess of benzoyl chloride acting on alcohol. When the portion obtained upon concentration was repeatedly fractioned, it could be separated into portions melting approximately at 193°, and others melting almost completely from as low as 135° to 155°. There seemed to be a tendency, however, for these lower fractions to liquefy at 142°–144°, and once, from an alcoholic solution of a fraction melting at 140°–150°, that evaporated at ordinary temperature, short, thick, prismatic crystals separated from the curved needles of the higher melting (193° C.) fraction. These few prisms melted at 144° C. without decomposition. An analysis of the body liquefying at 193° gave the following figures:

0.2277 gram, dried over H_2SO_4, gave 0.5785 gram CO_2 and 0.0945 gram H_2O.

0.2001 gram gave 10 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.30
H	4.60	4.61
N	5.82	5.85

An analysis of a fraction melting from 145°–165° gave these percentages:

0.1421 gram, dried over H_2SO_4, gave 0.3635 gram CO_2 and 0.0565 gram H_2O.

0.6726 gram gave 34.1 cc. N at 15° C. and 770 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.74
H	4.60	4.43
N	5.82	6.02

The benzoyl ether is not at all soluble in water or ligroïn, is slightly soluble in cold alcohol, but dissolves readily in ether, chloroform, and glacial acetic acid. The low-melting body seems to be more soluble in alcohol than its higher-melting isomer, but, as nine-tenths of the total product appeared to be the body melting at 193° C., the small proportion of the low-melting compound may account partially for the idea that the latter is more soluble.

From Toluquinone.—The oxime was made according to the method of Goldschmidt and Schmidt,[1] by treating toluquinone in aqueous solution with an excess of hydroxylamine hydrochloride, extracting with ether, and purifying with animal charcoal. From the sodium salt of the oxime thus formed the benzoyl ether was made in the manner previously described. The product is identical with the benzoyl ether made from *o*-cresol. The body melting at 193° C. was readily isolated and analyzed:

0.1002 gram, dried over H_2SO_4, gave 0.2565 gram CO_2 and 0.0452 gram H_2O.

[1] Ber. d. chem. Ges., **17**, 2063.

0.3581 gram gave 17.8 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.81
H	4.60	5.01
N	5.82	5.77

By fractional crystallization, low-melting portions were separated, exactly as in the case of the benzoyl ether made from *o*-cresol, except that some fractions were obtained melting partially as low as 129° C. In order to be certain that benzoic acid (m. p. 120° C.) was not unduly lowering these melting-points, these fractions were boiled with water and filtered hot. The filtrate was not acid to litmus and contained only a trace of organic matter. The ethers, when dried, gave the same melting-point as before boiling with water, and, upon recrystallizing from a little alcohol, did not exhibit any change. Furthermore, the benzoyl ether obtained by the usual method, when only 75 per cent. of the theoretical quantity of benzoyl chloride was used, gave fractions beginning to melt at 129° C. Obviously benzoic acid could not be present in these instances.

By slow, spontaneous evaporation of the alcoholic solution of a fraction liquefying at 140°–150° C., a few crystals melting at 142° C., similar to those obtained in the same manner from the oxime made from *o*-cresol, separated from the body melting at 193° C. Since there was not enough of this compound for a combustion, an analysis was made of a fraction melting at 137° C. with the following results:

0.1131 gram, dried over H_2SO_4, gave 0.2901 gram CO_2 and 0.0480 gram H_2O.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.96
H	4.60	4.72

Fractions were frequently obtained melting at about 177° C., and from these attempts were repeatedly made to isolate some of the ortho isomer. None was ever detected under the lens, and fractional crystallization always separated such por-

tions, principally into the body melting at 190° C., and a small fraction melting much lower.

Since the benzoyl ether will decompose into a dark-brown liquid with the evolution of brown fumes of nitrogen oxides when heated above 160° C., it is only by rapidly heating that 193° C. can be observed as a melting-point. This applies also to the bromine addition-products of the benzoates of both the ortho- and metaoximes.

Dibromtoluquinone-m-oxime Benzoyl Ether.

The benzoyl ether was dissolved in chloroform and cooled while the theoretical quantity of bromine was added in small portions. After standing for an hour, the chloroform was evaporated spontaneously, and the light-brown residue recrystallized from glacial acetic acid. It can also be purified by dissolving in fuming nitric acid and pouring into water. On analysis:

0.1437 gram, dried over H_2SO_4, gave 0.2176 gram CO_2 and 0.0339 gram H_2O.

0.1215 gram gave 0.1140 gram AgBr.

	Calculated for $C_{14}H_{11}Br_2NO_2$.	Found.
C	41.90	41.30
H	2.76	2.62
Br	39.87	39.93

The dibromide is insoluble in water, somewhat soluble in cold alcohol, and readily dissolves in chloroform and glacial acetic acid, from which it crystallizes in white prisms melting at 165° C. with decomposition.

Monobromtoluquinone-m-oxime Benzoyl Ether.

When the dibromide is boiled with alcohol hydrobromic acid splits off, two hours being required to complete the process, during which little or no saponification takes place. After recrystallizing from alcohol, a mixture of monobrom compounds is obtained, melting from 155°–170° C. A portion melting with decomposition at 174° C., was separated and analyzed:

0.1208 gram, dried over H_2SO_4, gave 0.2319 gram CO_2 and 0.0345 gram H_2O.

0.0735 gram gave 0.0425 gram AgBr.

	Calculated for $C_{14}H_{13}BrNO_3$.	Found.
C	52.49	52.36
H	3.15	3.17
Br	24.98	24.63

It is very similar in its properties to toluquinone-*m*-oxime benzoyl ether, crystallizing from alcohol in bright-yellow needles.

Toluquinone-o-oxime Methyl Ether.

The methyl ether of toluquinone-*o*-oxime was made from the silver salt and methyl iodide in the same manner as its meta isomer, the yield being somewhat better. Once recrystallized from ligroïn:

0.1247 gram of the ether, dried over H_2SO_4, gave 0.2931 gram CO_2 and 0.0675 gram H_2O.

0.3484 gram gave 27 cc. N. at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	64.10
H	6.00	6.01
N	9.29	9.22

Its properties are almost identical with the methyl ether of the meta form. It crystallizes from ligroïn in long yellow needles, every portion of which, obtained by fractional crystallization, melts at 69° C.

Dibromtoluquinone-o-oxime Methyl Ether.

The methyl ether was dissolved in chloroform, cooled, and the calculated quantity of bromine added. The reaction is completed in twenty minutes, and, on evaporation of the chloroform, the dibromide is left behind as a dirty white mass. Once recrystallized from ligroïn, the substance is ready for analysis:

0.1690 gram, dried over H_2SO_4, gave 0.1877 gram CO_2 and 0.0456 gram H_2O.

0.0744 gram gave 0.0909 gram AgBr.

	Calculated for $C_8H_5Br_2NO_3$.	Found.
C	30.87	30.29
H	2.92	3.00
Br	51.41	52.00

It is insoluble in water but quite soluble in most organic reagents. From ligroïn it crystallizes in white prisms, melting at 112° C.

Toluquinone-o-oxime Acetyl Ether.

This ether was made by Wurster and Riedel[1] from toluquinone-*o*-oxime and acetic anhydride. It can be prepared also from the silver salt and acetyl chloride, the yield being very poor, only a trifle better than its meta isomer, which it closely resembles in its properties.

0.1194 gram, dried over H_2SO_4, gave 0.2666 gram CO_2 and 0.0545 gram H_2O.

0.2389 gram gave 15 cc. N at 15° C. and 760 mm. pressure.

	Calculated for $C_9H_9NO_3$.	Found.
C	60.30	60.89
H	5.06	5.07
N	7.84	7.35

From ligroïn it crystallizes in irregular yellow prisms, melting at 92° C.

Toluquinone-o-oxime Benzoyl Ether.

This ether was made in alcohol solution from the sodium salt in the manner already described for the benzoyl ether of the meta form. The yield is practically theoretical, and, after one recrystallization from alcohol, the product is ready for analysis.

0.1589 gram, dried over H_2SO_4, gave 0.4074 gram CO_2 and 0.0686 gram H_2O.

0.5101 gram gave 26.1 cc. N at 15° C. and 766 mm. pressure.

[1] Ber. d. chem. Ges., **12**, 1799.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.92
H	4.60	4.80
N	5.82	6.04

Although submitted to the most careful fractional crystallization, every particle obtained melted sharply at 177° C., with slight decomposition. From alcohol it crystallizes in light, brownish-yellow blades, which have all the properties of the metaoxime benzoyl ether except that it is a little more soluble in organic reagents.

Dibromtoluquinone-o-oxime Benzoyl Ether.

The benzoyl ether was dissolved in chloroform, bromine added to the cooled solution, and the product recrystallized from glacial acetic acid.

0.2111 gram, dried over H_2SO_4, gave 0.3208 gram CO_2 and 0.0564 gram H_2O.

0.1003 gram gave 0.0924 gram AgBr.

	Calculated for $C_{14}H_{11}Br_2NO_3$.	Found.
C	41.90	41.44
H	2.76	2.97
Br	39.87	39.21

It is insoluble in ligroïn and water and but little soluble in cold alcohol. Fuming nitric acid dissolves it readily, and from the solution it is precipitated unchanged by water. It crystallizes from glacial acetic acid in short, thick, orthorhombic prisms melting at 159° C. with decomposition.

THE KENT CHEMICAL LABORATORY
of YALE UNIVERSITY,
June, 1898.

ON THE CLAIMS OF DAVYUM TO RECOGNITION AS A CHEMICAL ELEMENT.

BY J. W. MALLET.

In the year 1877, the Russian chemist, Sergius Kern, announced[1] that in treating native platinum ore he had detected a new metal of the platinum group, which he proposed to name in honor of Sir Humphry Davy. A brief description

[1] Compt. rend., **85**, 72; Chem. News, **36**, 4, 114, 155, 164; and **37**, 65.

was given of the process by which the separation of the metal was effected, and some of its reactions were described. The metal itself was said to be silvery in appearance, fusible with difficulty by means of the oxy-hydrogen blowpipe, hard, and to some extent ductile, of spec. grav. 9.385 at 25° C. Only 0.27 gram was obtained from 600 grams of the platinum ore, = 0.045 per cent., and in subsequent papers the author spoke of it as still more sparingly obtainable, saying that most of the platinum ore used contained but 0.0008-0.001 per cent., that only a few samples gave as much as 0.035-0.045 per cent., and that the whole quantity of davyum obtained was "so small that no serious experiments could be made." The only report by another chemist on the existence of this claimant for distinct elementary character seems to be a very short paragraph in Valentin's "Course of Qualitative Chemical Analysis (6th edition, 1884), in which the editor, Dr. W. R. Hodgkinson, says that he has obtained a small quantity of the new metal from native platinum, and has found that "it decomposes water in presence of H_2SO_4, the oxide formed scarcely dissolving in the acid"—a very remarkable statement in regard to a metal of the platinum group.

Most compilers of chemical handbooks have either ignored davyum altogether, or have relegated it to mere mention among the sundry "supposed elements," of which the list is not a short one. It is desirable that this list be as far as possible expurgated, and any experiments tending to establish or overthrow belief in the existence of a supposed element have some interest.

The point which seems to make it particularly interesting to decide whether there is such a metal as davyum or not, is the statement by Kern that the atomic mass, as determined in preliminary experiments by Alexejeff, must be near to 154. This would suggest the possible existence in the "periodic" classification of the elements of a hitherto unrecognized element, or more probably a triad of elements, analogous to the triads—ruthenium, rhodium, palladium, and osmium, iridium, platinum,— and having an average atomic mass about

half way between these two sets of three. Thus we should have:

Ruthenium 100.91	?	Osmium 189.55
Rhodium 102.23	Davyum 154.?	Iridium 191.66
Palladium 105.56	?	Platinum 193.41

It is noteworthy that in Mendeléeff's arrangement of the elements in groups and series, we have representatives of the eighth group in the fourth, sixth and tenth series, but none in the eighth series, a place which would be taken by elements with atomic masses approximately equal to that attributed to davyum. So that, if the existence of davyum were established, it would render probable the subsequent discovery of two more metals analogous to it.

As the best means of securing a favorable chance for investigating the existence or non-existence of the supposed element, I wrote two or three years ago to Mr. George Matthey, F. R. S., of London, knowing the generous readiness to aid scientific research which he and the eminent firm of platinum manufacturers to which he belongs have always shown. I stated to him the object which I had in view, and asked whether he would be willing to let me have the use of such residues from the working on the large scale of native platinum as might most probably yield davyum, any of the already known platinum metals separated therefrom to be returned. His reply was most cordial, and he obligingly offered the free use of such residues as I should designate. The feature in Kern's description of his new element which seemed to offer the best starting-point was the very slight solubility of the double chloride of davyum and sodium, and I suggested to Mr. Matthey that if, without too much trouble or disturbance of the usual course of working native platinum, the solution in *aqua regia* of the crude material, cleared by decantation from the insoluble osmiridium, etc., and by precipitation with ammonium chloride from the bulk of the platinum, could be evaporated to dryness with a large excess of common salt, and the residue redissolved in a minimum of water, any sparingly soluble material left behind by this second solution might be expected to contain the element

sought for, and should be collected and sent to me. He very kindly promised that this should be done, but it was not feasible to take up the matter for some months. Meantime Mr. Matthey informed me that in the precipitation of platinum from certain liquors, a solution of ammonium chloride saturated with sodium chloride was often used, and that by evaporation of the clear solution (after precipitation) colored crystals of impure sodium chloride with a little ammonium chloride were produced; this crude salt he thought might be worth examination, and he offered to send me some of it. In due time I received about a pound of this rose-colored common salt, and later a specimen of the residue obtained by treating a lot of native platinum as I had suggested—35 kilograms[1] of Russian platinum mineral had yielded 13 grams of residue, and of this about half was sent me. Mr. Matthey stated in a letter accompanying the sample of residue that the process had been unusually tedious, in consequence of the fact that in the second crystallization, when the liquor was saturated with sodium chloride, such a dense mass of crystals formed to be redissolved only by the cautious use of cold water, as to require a very long time for solution and settlement. The two materials for examination, therefore, were this residue, obtained in accordance with my suggestion as to treatment of the complex solution of the metals from native platinum with sodium chloride, and the rose-colored crystals of impure common salt from the regular course of procedure offered me by Mr. Matthey.

It was at once apparent on inspection of the former of these —the residue from special treatment—that it was not likely to be the sodio-chloride of any metal. It was an exceedingly fine gray powder, with minute glistening specks, and proved to be insoluble, not only in water, but in ordinary acids. It was hard enough to readily scratch glass, and even made some minute scratches upon rock crystal, when rubbed on by means of cork or wood. Seen under the microscope it exhibited a multitude of transparent, colorless granules, with

[1] This quantity, at the lowest proportion reported by Kern, *viz.*, 0.0008 per cent., should have contained 0.280 gram of metallic davyum, or at the highest proportion reported, 0.045 per cent, 15.750 grams.

a smaller proportion of steel-gray or black, opaque and brilliantly lustrous little crystals, most of which were hexagonal plates with (plane) angles of 120°, and a few angles which measured a little more than 127°. Many fragmentary crystals were visible, and a few had the appearance of elongated blades. Many of the perfect crystals, while very minute, were beautifully sharp and well defined. Treatment with gently heated hydrofluoric acid drove off much silicon fluoride, and heating of what remained with concentrated sulphuric acid rendered soluble a small amount of zirconium sulphate with a trace of iron. The residue from the action of both acids was mixed with sodium chloride in fine powder, and at a dull red heat exposed to the action of moist chlorine gas—this, Wöhler's process for decomposing osmiridium, proved easily effective in consequence of the fine state of division of the material, and yielded osmium volatilized mainly as the tetroxide, and iridium with a little rhodium left behind as sodio-chloride. It was evident that the material sent from London consisted merely of such part of the insoluble matter of the native platinum as *aqua regia* had left behind in so extremely fine a state of subdivision that it had remained suspended through the no doubt careful settling and decantation to which the platinum solution had been subjected. It is interesting to find so very dense a substance as osmiridium thus long held in suspension. After deduction of rather more than one per cent. of hygroscopic moisture, the composition of this residue was approximately

Quartz	40.8			
Zircon	15.4			
Osmiridium	43.8	= about	Iridium 30.2 Rhodium 1.4 Osmium 12.2	(decomposition by chlorine not quite complete).
	100.0			

The crude common salt in rose-colored crystals dissolved almost completely in water, producing a solution of rather orange or aurora-red color, having a distinct, though not very strong, acid reaction to litmus. Using a minimum quantity of cold water, applied in several successive portions, a minute residue was left undissolved, but a few milligrams

from a couple of hundred grams of the salt, which residue consisted partly of fine light gray matter resembling that already noticed, but chiefly of a buff-colored powder, appearing under the microscope (with a power of 250–450 diameters) as distinctly transparent and crystalline, with the general aspect of minute octahedra and cubo-octahedra; no colors shown in polarized light. The clear aqueous solution was reduced by a rod of extremely pure zinc, and a little hydrochloric acid. Most of the metallic precipitate thrown down was loose and flocculent, but there was a strong tendency to the formation of a *specular* and pretty firmly adherent deposit on the glass of the beaker and stirring rod. The precipitate, dried at 120° C., represented a little less than 0.2 per cent. of the crude salt taken. This precipitate, which if strongly ignited in the air gave off a slight but unmistakable odor of osmium tetroxide, was redissolved by *aqua regia*, and the solution was mixed with a moderate excess of sodium chloride, evaporated almost to dryness, rediluted with water and again evaporated to remove surplus acid, and finally allowed to stand in the cold for two or three days, the concentration being such that only a little sodium chloride separated out. On decanting, and cautiously removing by water the small remaining surplus of sodium chloride, a little more of a buff-colored residue was obtained, looking, both to the naked eye and under the microscope, like the original residue from the treatment of the crude rose-colored salt with water. The buff-colored material from these two sources —that first obtained having been freed from the light gray powder by washing with a saturated solution of common salt, and decantation—was washed with alcohol, in which it seemed to be practically insoluble, and dried. A little specimen of it dissolved in a large quantity of water. Another small portion, tested spectroscopically, showed the presence of sodium with a trace of potassium. The principal part was dried at 120° C., weighed, and heated to redness in a stream of hydrogen; the residual metal, washed free of alkaline chloride, was dried and weighed; it formed 37.1 per cent. of the salt decomposed. Assuming this double chloride to be

anhydrous, sodium to be the only alkaline metal present, and a single metal of the platinum group to be associated with it, the atomic mass of such platinum metal would be 151.5 for the formula Na_2MCl_6, or 165, for the formula Na_4MCl_6. Of these formulæ the former is the more probable, and leads to an approximate value for the atomic mass not very different from that assigned by Kern to davyum. Both determinations were made with quantities altogether too small for any very accurate result.

The general properties of the metallic material thus obtained agreed in the main with those described by Kern, as far as they could be compared by experiments on so minute a scale, and after solution in *aqua regia*, which was effected but slowly and with difficulty, the reactions in the liquid way were pretty nearly such as he obtained. But, although a small part of the solution gave a red coloration with potassium thiocyanate, a reaction pointed out by Kern as among those particularly characteristic of davyum, a simple additional test with potassium ferrocyanide at once showed the presence of iron, though in small amount, thus accounting for the red color. Furthermore, on placing, in the chief portion of the solution, a little lump of sal ammoniac and allowing it to remain until it had dissolved to saturation, a dark brown-red precipitate was formed, from which the ordinary reactions of iridium were obtained, while the remaining liquor, evaporated to dryness and the solid residue ignited, left rhodium, probably not pure, but identifiable by the action upon it of fused potassium acid sulphate. So that the material examined consisted, not of a single distinct metal, but merely of a mixture of iridium and rhodium with a little iron. The whole quantity available was quite insufficient for any exact quantitative analysis, but the very rough approximation to a mean atomic mass indicates that the two metals of the platinum group must have been present in not very unequal quantities.

Of course the results thus obtained, while lending no support to a belief that there is such an element as davyum, do not suffice to disprove its existence. It may, however, be

remarked that in the account given by Kern himself of his experiments, there are some points tending to increase doubt as to the conclusion which he reached. Thus, there is, probably from carelessness, some erroneous statement of facts, as, for instance, the assertion that *like platinum chloride* the chloride of davyum forms double salts with ammonium and potassium chlorides *insoluble in water and easily soluble in absolute alcohol.* It is suggestive that davyum is said to have been obtained from native platinum in the separation of rhodium and iridium. There is no allusion to the well-known fact of the reactions afforded by one of the platinum metals being modified by the presence along with it of others of this group, notably true of iridium solutions when containing also platinum, palladium, or rhodium. It is unsatisfactory to find the statements that "careful qualitative analyses showed no presence whatever of iron," and that the author's davyum "was found to contain no metals of other groups" without any details being given of the tests by which it was supposed that these points were established.

On the whole it seems most probable that, in default of better proof of elementary character than has yet been given, davyum is to be looked upon as merely a mixture of iridium and rhodium with a little iron; and, hence, that we have not yet reason to believe in the existence of a third triad group of platinum metals.

UNIVERSITY OF VIRGINIA,
August 20, 1898.

REVIEWS.

THE DISCHARGE OF ELECTRICITY THROUGH GASES. Lectures delivered on the occasion of the sesquicentennial celebration of Princeton University. By J. J. THOMSON, Professor in the University of Cambridge. New York: Charles Scribner's Sons. 1898. $1.00.

The authorities of Princeton College, in the fall of 1896, in honor of its sesquicentennial and to commemorate its transition from a college into a university, invited some of the noted scholars of Europe to attend these exercises and to deliver courses of lectures on their special subjects. Among those who accepted the invitation were Professors Dowden, of Trinity College, Seth, of Edinburgh, Klein, of Göttingen, and J. J.

Thomson, of Cambridge. The latter delivered four lectures and has now published them in an expanded form with some results obtained since the lectures were delivered. The book is illustrated with diagrams and is in the form of a continuous treatise and not of separate lectures. It is divided into three parts: The Discharge of Electricity through Gases, containing the various methods of electrification of gases; Photo-electric Effects, under which head he takes up the different forms of sparks, conductivity the arc in hydrogen and the transport of one gas through another; and Cathode Rays. Under this special form of transmission, to which so much attention is now being given, the author discusses, among other things, the effects produced by these rays, their properties and the influence of outside agents on them, and the theories of the nature of cathode rays. He considers the phenomena best explained on the assumption that the rays are composed of corpuscles in motion, the corpuscle being formed by the breaking up of atoms, a theory which, if sustained, will destroy the theory, held for so long, of the indivisibility of atoms. No further recommendation of this book is necessary than the mention of the name of the author, who is so well known for his scientific investigations and writings. It is a summary in a form suitable for one who is not a specialist. J. E. G.

JAHRBUCH DER ELEKTROCHEMIE. NERNST UND BORCHERS. Jahrgang 1897. Halle: Wilhelm Knapp. 1898. 15 Marks.

Meyer's Jahrbuch der Chemie contains a brief mention of the investigations, in the different branches of chemistry, carried on each year; but this science has become specialized to such an extent that it has been found impossible to cover the ground in detail in such a volume, and works devoted to special subjects have been established to supply this need. In 1893 a Jahrbuch der organischen Chemie was started, and in 1894 the development of Electrochemistry had been so great as to necessitate the publication of a Jahrbuch der Elektrochemie to cover all the work in this line. The present volume is the fourth in this series, and its size cannot fail to impress one with the great advance made in this special branch of chemistry within a few years. All the investigations, in the line of electrochemistry, which have been carried out during 1897 are fully treated in this number, which is a valuable addition to those already published. J. E. G.

A BRIEF COURSE IN QUALITATIVE ANALYSIS. By E. A. CONGDON, PH.B., F.C.S. Professor of Chemistry in the Drexel Institute, Philadelphia, Pa. New York: Henry Holt & Co. 1898.

The author has aimed, in this book, to make the matter

"as concise as possible with the least sacrifice of a study of reactions and solubilities of chemical importance," and for this reason "many of the reactions found in larger books have been omitted." The matter is arranged in groups, each one being taken up in turn, the characteristic precipitates discussed in order, and methods given for the separation of the members of the group and of the groups from one another. There is no new feature in the book, as it is only one of the many arrangements of the same material made by various teachers to serve their special needs. J. E. G.

EXPLOSIVE MATERIALS: THE PHENOMENA AND THEORIES OF EXPLOSION AND THE CLASSIFICATION, CONSTITUTION, AND PREPARATION OF EXPLOSIVES. By CAPTAIN J. P. WISSER, 7th Artillery. Instructor, Department of Military Science, United States Artillery School. New York: D. Van Nostrand Co. 1898. 16mo. 50 cents.

The first edition of this work appeared fifteen years ago, and the present edition has been entirely rewritten and brought up to date. For a general résumé of the nature and causes of explosions, the chemical composition of the explosives, the nature of the chemical acts involved, and the composition of all known explosives this book will serve as a handy reference. It is well written and attractive and contains a well arranged index and references to the larger works on this subject. It is one of the numbers of the Van Nostrand Science Series, and is sufficiently small to be carried in the pocket. J. E. G.

ELEMENTS OF GENERAL CHEMISTRY WITH EXPERIMENTS. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry and Director of the Chemical Laboratories in the Schools of Medicine and Pharmacy of Northwestern University. Chicago: E. H. Colegrove. 1898.

The author has prepared an excellent book which can be recommended as a valuable guide for elementary classes in chemistry. The matter is well arranged and the descriptive part is clear and not filled with unnecessary details. It is intended as a classroom and laboratory guide, the statements made being verified wherever possible by experiments for which explicit directions are given. The author has avoided the mistake so often made of plunging the student at once into a consideration of theories which cannot be understood without a groundwork of experimental results, and he has treated the atomic theory from an historical point of view. The book is well printed and bound, and attractive in every way. J. E. G.

A TEXT-BOOK OF ELEMENTARY ANALYTICAL CHEMISTRY, QUALITATIVE AND VOLUMETRIC. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry and Director of the Chemical Laboratories in the Schools of Medicine and Pharmacy of Northwestern University. Chicago: E. H. Colegrove. 1898. Price, $1.50.

This book is intended principally for the use of students of

medicine and pharmacy. The part devoted to qualitative analysis contains, beside the matter usually presented in such courses, methods for the detection of some common organic substances and poisons. The second part of the work is devoted to volumetric analyses as the author thinks that more knowledge can be gained, in the same length of time, by these methods than from the study of gravimetric ones. The general principles of volumetric analysis, the method of preparing the solutions, analyses by neutralization, precipitation and oxidation, the determination of sugar and related substances, the volumetric methods used in water analysis and the use of the nitrometer are considered in this part. This course, which is mapped out, should give the student a good general knowledge of the methods of volumetric analyses; but if, as in many of the medical schools is no doubt the case, the course in chemistry is not pursued any further, it would perhaps be more satisfactory to omit a part of this course and substitute a few typical cases of gravimetric methods. J. E. G.

A LABORATORY GUIDE IN QUALITATIVE CHEMICAL ANALYSIS. By H. L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New York: John Wiley & Sons; and London: Chapman & Hall. 1898.

This volume, of 154 pages, adds another to the many already existing manuals of qualitative inorganic analysis for use by beginners. Most of the facts and directions based upon them are of course substantially the same as those to be found in numerous other books having the same object in view.

A point deserving praise is the detailed study required from the experimenter of the exact behavior of given solutions with reagents, observing the effects of varying dilution, temperature, etc.

On the other hand, there is some ground for adverse criticism in the instructions with respect to "chemical equations", to which a separate chapter is devoted.

Such an expression as the following: "Thus, $Ag + Cl' = \underline{AgCl}$, shows that solutions of any silver salt and any chloride when mixed (in neutral or acid solution) give a precipitate of silver chloride", is not only open to objection as too sweeping a statement in point of fact, but is liable to suggest to the beginner the too common idea that the formula found in the text-book is the *cause* of the phenomenon observed in the test-glass. The list is a very restricted one of the substances examined and the reactions used for their detection. J. W. M

A SHORT COURSE IN INORGANIC QUALITATIVE ANALYSIS. For Engineering Students. By J. S. C. WELLS, Ph.D., Instructor in Analytical Chemistry, Columbia University. New York: John Wiley & Sons; and London: Chapman & Hall. 1898.

In the main the remarks made as to the work last noticed

apply also to this one. It is evidently intended for use by the author's pupils, and much oral explanation would be necessary to make it practically available, so that it can hardly be regarded as an independent treatise. For example, on p. 267, the student is told that in making a preliminary examination of the material before him he should "heat a portion gently with oxidizing flame upon charcoal." No doubt a blowpipe flame is meant, but nothing has been said about the blowpipe or what an oxidizing flame is. Lack of accuracy and clearness in the language used is likely to puzzle a beginner. Thus, on p. 9, having given as an example of an equation

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$

the author says: * * * * * * * * * "This brings us to another important property of symbols, *viz.*, that they not only represent the elements themselves, but they also represent their atomic weights, as compared with the atom of hydrogen which is taken as the unit." How the tyro is to find the atomic weights of the elements referred to in the equations from the symbols given is not easy to see. And, on p. 12, in reference to the equation

$$2FeCl_2 + Cl_2 = Fe_2Cl_6$$

it is remarked: "Although oxygen does not enter into the reaction, we say that $FeCl_2$ has been oxidized." Such sentences are not likely to help the student along.

Sydney Smith is reported to have said of a man, who in a moment of impatience at a long-winded account of Arctic exploration had "damned the North Pole," that he had also gone so far as to "speak disrespectfully of the Equator." One is sometimes sorely tempted to use strong language in regard to *Equations*, in view of the misuse too often made of them in connection with chemical teaching.

In neither of the two books just noticed does reference seem to be made to a small stumbling block which students of analytical chemistry need to be guarded against; namely, that arising from the almost universal presence in materials examined of "traces" of foreign substances in a state of accidental mixture. It is clearly desirable that work be not restricted to laboratory products in a condition of so-called purity, but that natural minerals, industrial products, etc., be also examined, and in these traces of non-essential iron, sodium, chlorine, etc., will frequently present themselves, making it needful that the student be taught how to judge *for himself* as to such traces, neither neglecting them altogether nor considering them as necessary constituents of the materials analyzed. J. W. M.

OBITUARY NOTICES.

J. A. R. NEWLANDS, whose name is so well known to chemists on account of the important part he played in the development of the Periodic System, died in England, July 29, 1898, at the age of sixty. In a book published by Mr. Newlands in 1884, all the papers published by the author on the question of the periodic arrangement of the elements were reprinted and his claim to priority in the matter defended. The first paper on the subject appeared in the *Chemical News* of Feb. 7, 1863, and was followed at short intervals by others on the same subject. Owing to the confusion prevalent then as to the correct atomic weights and to inconsistencies and inaccuracies in the arrangement, the "Law of Octaves" did not receive the attention it merited, and it was not until the papers of Mendeléeff and Lothar Meyer appeared that the great importance of the Periodic Law was realized. Mr. Newland's claim as the originator of the idea has, however, been generally recognized, and in 1887 he was awarded the Davy Medal of the Royal Society, in recognition of his work on the Periodic Law of Elements. Mr. Newlands did very little work in the field of pure chemistry, but devoted himself to the industrial side of the subject and especially to the sugar industry.

J. E. G.

In the death of the Right Hon. Lord PLAYFAIR, K.C.B., F.R.S., which occurred May 29, 1898, the Chemical Society of England lost one of its oldest and most prominent members and an ex-president. He was 79 years old and had always taken a great interest in scientific questions. When 19 years old he went to Giessen and studied under Liebig and was appointed professor of chemistry in the Royal Institute at Manchester in 1843. After serving on a number of commissions appointed for the study of important sanitary measures for the kingdom, he was appointed professor of chemistry at the University of Edinburgh. He also served on several Royal Commissions, occupied the office of Postmaster-General, and held important offices in the House of Commons. The honors and titles to which he attained were marks of the appreciation in which he was held by the people for the beneficial results of the application of his wide and thorough scientific knowledge to questions of paramount importance to the nation. J. E. G.